A
SYSTEM
OF
CHEMISTRY.

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SYSTEM

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CHEMISTRY.

THE substances which are formed in the Vegetable and Animal Systems, and which are to be the subjects of consideration in this volume, are all compounds. From the nature of their chemical constitution, they derive peculiar characters, by which they are connected with each other, and are discriminated from the compounds which belong to the mineral kingdom.

With regard to composition, the mineral substances are extremely varied as to the principles of which they are composed, but simple as to the modes in which these are combined. All the simple substances are to be found in the mineral kingdom, but they are generally united in binary combinations, or, by the un[illegible] pounds, others are formed. Th[illegible] hand, which are formed in th[illegible] systems, are more uniform with regard to the principles of which they are composed, but more diversified in the modes in which these are combined : they consist only of [illegible]nts, which are united scarcely ever in binary, [illegible] ternary, quaternary, or even more-complica[illegible]tions ; and from differences in the proportion[illegible] modes of union, arise the extremely diversified [illegible] by which they are distinguished. All the veg[illegible]ducts may be said to consist of carbon, [illegible]ogen[illegible] oxygen ; the animal, of carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulphur. Some of the metals and earths, particularly iron, manganese, gold, silex, and lime, and the fixed alkalis, are likewise obtained from vegetable and animal bodies. But the quantities of these are seldom considerable : some of them are perhaps formed during the analysis by which they are obtained, and others may be regarded as foreign substances accidentally introduced. Lime and iron are of these principles the most constant, and present in largest proportion.

From the nature of the composition of these substances, arise the chemical properties by which they are characterized. The compounds of the mineral kingdom, consisting, in general, of two immediate principles, united by a single affinity, have no tendency to suffer spontaneous changes ; or, when left to themselves, there is no cause to disturb the uniformity of their mutual attraction. The relative force of attraction by which their principles are united, can also be in some measure estimated, and the circumstances by which that attraction is modified determined ; hence, by presenting these principles to each other under these circumstances, we can effect their combination, or form compounds possessed of precisely the same properties. We can analyse these compounds with equal facility, or, by a simple decomposition, separate their principles, so as to obtain them isolated. We can therefore ascertain with accuracy their composition, both as to the nature and proportions of their constituent parts, and as to the modes in which these are combined.

But the chemical constitution of the vegetable and animal products is extremely different, and gives rise to very different chemical characters. As they always consist of three or more principles, which have strong mutual attractions, the balance of these attractions, whence any particular compound exists, is easily subverted; the principles have a perpetual tendency to re-act on each other, and enter into new combinations,—a tendency rendered effectual by the slightest alteration of circumstances. Hence arises the facility of decomposition which is characteristic of these bodies: they are liable to spontaneous changes, fermentation and putrefaction: they are readily acted on by other agents, as by water or atmospheric air; and they are totally changed by an increase of temperature. As their principles, too, have mutual affinities of nearly the same force, they never escape from a combination pure and uncombined, but unite with each other, forming a complicated analysis; and as their composition, with regard to the ultimate principles, is much alike, the products of this analysis, in the different individual substances, are extremely similar. And, lastly, as we are incapable of balancing the attractions of the several principles of which they are formed, or of placing these principles under the circumstances under which they were brought into union in the vessels of the animal or plant, we can seldom, by artificial arrangements, form compounds of a similar nature.

Such are the chemical properties which peculiarly distinguish the products of organization,—their susceptibility of decomposition, the complicated nature of their analysis and the similarity of its products, and the impracticability of their artificial formation from the direct union of their constituent principles.

There are some subordinate distinctions between the vegetable and the animal substances. As the constituent principles of animal matter are more numerous, their affinities are more nicely adjusted, and more liable to be altered by the slightest alteration of circumstances. Hence the animal products are, in general, more susceptible of decomposition. This, too, is of a nature somewhat different, with regard to the products, from that of vegetable matter; and, in particular, they are distinguished, by being liable to that species of spontaneous decomposition which constitutes putrefaction: the others decay, but their decomposition is not marked by the evolution of those products which distinguish that of animal matter, and which characterize this process. Their analysis by heat also is different. Vegetables are resolved principally into carburetted hydrogen, carbonic oxide, and carbonic acid: animal substances always afford a large quantity of ammonia, and generally also combinations of hydrogen with sulphur, phosphorus, and nitrogen. It is on the presence, principally of these three latter substances, that these differences depend: in vegetables, they are generally altogether wanting, or, if present, are always in inconsiderable proportion.

Though the compounds which belong to the vegetable and animal kingdoms can seldom be formed by artificial arrangements, it is not to be concluded, as has been done, that this arises from peculiar unknown forces, [illegible] exertion of which their natural formation [illegible] plished. They are chemical compounds, [illegible] of chemical affinities, which have been exerted in [illegible] under peculiar circumstances. We can even by artificial processes form compounds perfectly similar to some products of vegetation; and, although the actions by which the greater number of these products are formed can be only imperfectly imitated in our processes, we can still so far trace them, as to discover their theory, and the nature of the modifications to which they are subjected. Hence the natural formation of these substances is strictly a subject of chemical investigation; and vegetable and animal physiology, so far as it is connected with this, is a department of chemical science,—one which is at present the most defective and obscure, but in which the progress is perhaps the least limited, which may reach the highest perfection, and present the most important results.

BOOK VIII.

OF VEGETABLE SUBSTANCES.

THE Vegetable Substances being less complicated in their composition than those belonging to the Animal Kingdom, and affording likewise, in general, the materials from which the latter are formed, are first to be considered.

Their chemical history may be comprised under three divisions. Under the first, may be stated the facts connected with their natural formation, or the principles of vegetable physiology, so far as this is dependent on chemistry. Under the second, may be considered in detail the chemical properties and relations of the several vegetable products. And to the third, may be referred their general analysis, and the chemical changes they suffer, either spontaneously, or when placed under peculiar circumstances.

CHEMICAL PHYSIOLOGY

CHAP. I.

OF THE FORMATION OF VEGETABLE SUBSTANCES, OR THE CHEMICAL PHYSIOLOGY OF VEGETABLES.

IN entering on this interesting subject, it is necessary to give a concise view of the structure and functions of plants, at least in so far as these are related to the chemical processes carried on in the vegetable system, by which the numerous products of vegetation are formed.

THE structure of plants is, in many respects, analogous to that of animals. Compared, indeed, with that of the higher orders of these, it is much more simple: no organs are found corresponding to the brain and nerves, the heart, the digestive system, or the muscles; but even in the lower tribes of animals, all these organs are not uniformly present; and in the general frame of vegetables, we discover that arrangement which is in strict propriety named organized. There are solid parts through which vessels conveying fluids are distributed, and organs in which functions similar to those of animals are performed.

The organized structure of vegetables is, of course, best discovered in the larger and more perfect plants. These consist of a stem or trunk, which, at its insertion into the earth, divides generally into a greater or smaller number of branches, which form the root, and at its upper extremity terminates likewise in a number of branches, to which the leaves and parts of fructification are attached.

On making a transverse section of any of these solid parts, a difference of structure is observed. In the centre, we find a soft substance which is named the Pith; external to this is the Wood, more hard and compact; and over the whole is an outer rough covering, the Bark.

The Bark has been considered as composed of three parts,—the epidermis, or external rough covering, consisting of numerous layers; the cellular tissue or envelope beneath, composed of fibres interlaced so as to leave interstices, which appear to be filled with a softer matter of a green colour; and, lastly, the cortical layers next to the wood, and approaching to it in structure. Through these parts run innumerable minute vessels, which appear to perform the functions of absorption and transpiration, and perhaps of assimilation and secretion.

The Wood is much denser than the bark. It is fibrous in its texture, and is composed of layers or zones. During the growth of the plant, a new zone is formed annually; and as, in different seasons, the vegetation is more or less vigorous, these zones vary in density and size. Through these layers are distributed a number of vessels, both straight and spiral, running in a perpendicular direction, and others which run horizontally from the bark. The part of the wood which is next to the bark is softer than the central part, and has been distinguished by the name of Alburnum; and there is a kind of gradation from the wood through this to the internal bark.

The Pith, or Medulla, placed in the centre, is similar in texture to the wood, only softer, and more cellular. It is always most abundant and most succulent in young plants, and is diminished and nearly obliterated by age. It appears to be of little importance in contributing to the growth of the vegetable. Mr Knight made a section through the bark and wood into the shoot of a vine, so as to extract as much as possible of the medulla; but it continued to grow as well as other shoots, the medulla of which had remained uninjured *. He conjectures, that its office is principally to form a reservoir of moisture to the plant.

In herbaceous plants, these different parts are not distinct; the wood, in particular, is wanting, and the stem is composed of a kind of cellular membrane, covered with an epidermis more or less thin, and inclosing the pith.

Attached to the stem or branches of plants, are the Leaves. Their structure seems similar to that of the cellular tissue of the bark, or is fibrous and interlaced, covered on each surface with a very fine membrane, and having numerous vessels distributed through the substance of the leaf, and inosculating freely with each other. Numerous small points, connected with these, are scattered over the surface; which have been regarded by Hedwig as apertures by which absorption and transpiration are performed; by Saussure, as glands which secrete or prepare the proper juices of the plant. The superior surface of the leaf differs, in general, perceptibly from the infe-

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* Philosophical Transactions, 1801, p. 338.

rior surface. The former is more smooth and shining; the latter has more asperities; its colour is paler, and with less lustre; the last differences probably arising from a less free exposure to light. These surfaces perform different functions. By the under surface, or that next the earth, absorption principally is performed, as Bonnet established by numerous experiments *; water, or watery vapour, being taken in, when in contact with it, so as to prevent the leaf from decaying immediately, even when detached from the plant; and watery vapour from the atmosphere, or dew, being probably absorbed in the natural situation. By the same surface, transpiration appears also to be performed, as the experiments of the same author have proved. This has been confirmed by Mr Knight. He applied a plate of glass to the under surface of a large vine leaf, in connection with the plant; and at the end of half an hour, so much water had exhaled, that it ran off the glass when held obliquely: but on placing it in contact with the upper surface of the leaf, not the slightest portion of moisture appeared †. This surface appears principally destined to expose the fluid circulating through the leaf to the chemical agency of light, and probably to emit the aërial matter arising from the decomposition of the circulating sap. Ingenhouz has accordingly stated experiments, in which he found, that the leaves furnish an air containing more oxygen, when their upper, than when their under surface is exposed to the direct action of

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[*] Recherches sur l'Usage des Feuilles.

[†] Philosophical Transactions, 1803, p. 278.

light *. So well adapted are these surfaces to the performance of their respective functions, that when their position is reversed, the plant makes every effort to regain that which is natural to them, or rather which is best adapted to the functions they have to perform, as Bonnet has abundantly shown. The leaves of some plants even follow, in some measure, the course of the sun, presenting always their upper surface to the direct rays of light.

The leaves are the proper respiratory organs of plants. It is sufficiently demonstrated by experiment, as is immediately to be stated, that, by their medium, plants change the state of the surrounding atmosphere, or perform respiration; and that reciprocal changes are effected in the fluids which circulate through the vessels of the leaf; that these fluids are thus prepared for the formation of vegetable matter, and are returned by a peculiar set of vessels to the body of the plant. The importance of the functions the leaves perform, is sufficiently demonstrated by the fact, that when they are destroyed the plant soon decays and dies.

There is much difficulty in tracing accurately the vessels of plants, and particularly in observing their connections and terminations, and the course of the fluids they convey. Hence the different opinions that have been advanced with regard to them, and the degree of uncertainty in which the subject is still involved. Naturalists, however, have generally agreed in distinguishing three kinds;—the common vessels, or those which convey the common juice, or sap; the spiral vessels, which

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* Experiences sur les Vegetaux, tom. ii. p. 193.

principally accompany these; and the proper vessels, or those which convey the peculiar juices of the plant after they are formed. It is an interesting object of inquiry, to discover the course of these different kinds of vessels, their relations and connections, and the offices they perform.

The first of these, the common vessels, occur chiefly beneath the cellular tissue of the root, stem, and branches, or in the alburnum, and rise longitudinally from the root to the leaves and flowers: they are frequently of considerable size, and are easily discovered by immersing the root of a growing plant in a coloured vegetable infusion: it is soon observed to ascend in them, and may be traced to the leaf, and even into the vessels which enter the leaf at the foot stalk, and are distributed through it. They appear to absorb fluids from the soil; and there exist similar absorbent vessels which run from the epidermis in an oblique or horizontal direction.

The proper vessels are situated principally in the cellular tissue and internal bark: they appear always to descend from the upper parts of the vegetable towards the root, and to convey a fluid downward. This is proved by the facts, that a coloured liquid does not ascend in them, as in the common vessels, when the root of a growing plant is immersed in it, and that, when the stem or a large branch of a plant is cut across, the proper juice always issues from the upper margin of the incision, and the production of new matter to fill up the incision takes place principally from this margin. As the common vessels can thus be traced upwards from the root to the leaves, and the proper vessels descend in the opposite direction, it seems necessarily to follow, that the connection between them, or the relation of the one to the other, is established in the leaf; and accordingly this has of late been investigated with considerable success.

In the leaf of every plant, we perceive an abundant distribution of vessels. A large vessel or bundle of vessels enters from the stalk, which runs through the centre of the leaf to its apex, extending to very minute ramifications, which appear to communicate freely with each other.

Dr Darwin conjectured, that this central vessel, or bundle of vessels, is formed by the union of smaller sap vessels, and that it performs the office of a pulmonary artery, distributing the sap it conveys over the extensive surface of the leaf; and thus exposing it to the action of the air and light, from which it may suffer those chemical changes necessary to its further assimilation. From the extremities of the minute ramifications of this vessel, this fluid, thus changed in its composition, returns, he conceives, by other vessels which pass along the under surface of the leaf, unite at the footstalk, and form larger vessels, by which it is conveyed to other parts of the plant. And he states the following experiment, from which this appears to be proved:

"A stalk with leaves and seed-vessels of large spurge (Euphorbia helioscopia) had been several days placed in a decoction of madder, so that the lower part of the stem, and two of the undermost leaves were immersed in it. After having washed the immersed leaves in clear water, I could readily discern the colour of the madder passing along the middle rib of each leaf. This red artery was beautifully visible both on the under and upper surface of the leaf; but on the upper side many red branches were seen going from it to the extremities of the leaf, which on the other side were not visible, except by looking through it against the light. On this under-side a system of branching vessels, carrying a pale milky fluid, were seen coming from the extremities of the leaf, and covering the whole underside of it, and joining into two large veins, one on each side of the red artery, in the middle rib of the leaf, and along with it descending to the footstalk or petiole. On slitting one of these leaves with scissars, and having a common magnifying lens ready, the milky blood was seen oozing out of the returning veins on each side of the red artery in the middle rib, but none of the red fluid from the artery.

"All these appearances were more easily seen in a leaf of Picris, treated in the same manner; for in this milky plant the stems and middle rib of the leaves are sometimes naturally coloured reddish, and hence the colour of the madder seemed to pass further into the ramifications of their leaf-arteries, and was there beautifully visible with the returning branches of milky veins on each side.

"From these experiments the upper surface of the leaf appeared to be the immediate organ of respiration, because the coloured fluid was carried to the extremities of the leaf by vessels most conspicuous on the upper surface, and there changed into a milky fluid, which is the blood of the plant, and then returned by concomitant veins on the under surface, which were seen to ooze when divided with scissars, and which, in Picris particularly, render the under surface of the leaves greatly whiter than the upper one." This fluid, thus prepared, Dr Darwin adds, is expended in the various secretions, and in the growth and nourishment of the plant *.

This has been further investigated by Mr Knight, in his late researches on the structure and functions of vegetables. He found, that when he made a circular incision round the stem of a plant, removing completely the bark at the incision, so as to cut off the connection of the stem by the medium of the bark with the leaves, it did not grow nor shoot out branches below the incision, but grew as vigorously as usual above the incision. Hence he was led to conclude, that the sap rising from the root through the wood, is prepared in the leaves for assimilation, and returns by vessels descending through the bark, to be subservient to the nutrition of the plant. In conformity to this he found, that if the stem below the incision produced a new shoot, as sometimes happened, then the parts beneath connected with this shoot began to grow. Or if he made incisions in different parts around the stem, allowing a leaf to remain in connection with each part between two of the incisions, the insulated leaf acted like the shoot, and the part between it and the incision beneath grew; while, if similar incisions were made without any leaf being allowed to remain, no growth nor increase in the size of the wood was discoverable. On the other hand, by making a com-

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* Botanic Garden, Notes, vol. i. p. 450. 453.

plete circular incision in the bark, and by a perforation extracting the pith in the centre of a branch, thus leaving a communication between the leaves and roots by the wood, the leaves still continued to flourish,—a proof, that the vessels conveying sap to the leaves, ascend through the wood *.

Having formed this view, he endeavoured to trace the course of the sap into the leaf, and its return to the other parts of the plant.

The sap vessels are easily traced from the roots through the alburnum, to the young stalks or shoots; the object therefore was, to trace their progress beyond this. Having made circular incisions as above, in the bark of some annual shoots of the apple and of the horse chesnut, he placed the stalk of the shoot beneath these incisions, in a deeply tinged vegetable infusion, for a few hours. On then making transverse sections of the shoots, he found that the coloured liquid had passed up the pores of the wood beyond the incisions, and into the insulated leaves; but it had neither coloured the bark nor the sap between it and the wood; proving, that the fluid rises from the commencement of the branch, through the wood, towards the leaves; while it appears to return by vessels situated in the inner bark, which have no immediate communication with the vessels of the wood.

Mr Knight, on examining the leaves in the shoots subjected to this experiment, found in the apple, that the leaf is attached to the wood by three strong fibres or

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* Philosophical Transactions, 1801, p. 334. 338.

tubes, or rather bundles of tubes; one entering the middle of the leaf, the others being on each side of it. In the horse chesnut, there are seven or eight bundles of a similar kind of tubes in each leaf. Through these the infusion had passed, and communicated its colour through almost the whole of each leaf-stalk. These tubes Mr Knight considers as being different from the common or sap vessels in the alburnum: they commence a few inches below the leaf to which they belong, and become more numerous as they approach to it. To distinguish them, Mr Knight has given them the name of Central vessels: they extend to the extremities of the leaf, where they appear to terminate, and are every where surrounded with the spiral vessels, which appear to be appendages to them.

Lying parallel with these vessels and surrounding them, are another set of vessels which were colourless, and appeared to be conveying a different fluid. They seem to return the sap to the tree, for when a leaf was cut off which had imbibed a coloured infusion, the native juices of the plant flowed from these vessels apparently unaltered, as Dr Darwin had formerly observed. They descend through the inner bark, and appear to extend from the extremities of the leaves to the points of the roots.

In conformity to these views, Mr Knight gives the following view of the circulation of the fluids in plants, or of the progress of the common sap, and its return to the different parts, to supply matter for nutrition and the formation of new products.

The sap is absorbed by the common vessels originating from the extremities of the roots of the vegetable, and rises through the alburnum of the root, stem, and branches, propelled by the contractile power of the fibres which diverge from the pith to the bark, and press on these vessels; in the branches it passes into what are named the central vessels, and through them into the leaf-stalk, and ultimately into the leaf. There it is exposed, in the delicate ramifications of these vessels, to the action of the air and light, and is converted, in part at least, into the proper juice of the plant: this is conveyed by the proper vessels which have their origin in the leaf, which unite and descend through the internal bark. In its progress through these vessels, it probably undergoes further changes, and is ultimately converted into the solid matter of the plant, and into the products which it affords *.

The use of the spiral vessels, either in this circulation or in any of the functions of the vegetable, does not appear very obvious. They are found round the pith, in the slender branches, the leaf-stalk, and the petals of the flowers. They are always empty, and hence some have supposed them to convey air: others have supposed them to be absorbent vessels, and have accounted for their being generally found empty, from their contractile power, in consequence of which they immediately discharge the fluid they contain when cut. As they are found principally connected with the central vessels in

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* Philosophical Transactions, 1801, p. 351.; 1803, p. 286.; 1805, p. 100.

the young shoots, and as in any other part of the plant they appear hardened and nearly obliterated, Mr Knight considers them as appendages to these central vessels, and, by some mechanism, facilitating the propulsion of the sap into the leaf, and its distribution over it; the action of the fibres of the alburnum, by which the sap had been propelled through the stem, ceasing, as he supposes, where that of the spiral vessels commences.

In this general structure of vegetables, there exists a striking analogy to the frame of animals; and from this analogy, as well as from the functions they perform, it has justly been inferred, that they are endowed with similar vital powers. At one period indeed, it was attempted to account for the motions of vegetables from their peculiar mechanism, independent of any living power. The ascent of the sap was thus ascribed to capillary attraction in the sap vessels; and the movements of different parts of the vegetable, were supposed to depend on the mere elasticity of their fibres. But such causes are altogether inadequate. Capillary attraction is insufficient to account for the motion of the sap; the velocity with which it ascends; the great height to which it reaches; for its variable motion; or for its propulsion and discharge when the vessels are cut. Still less can it be assigned as the cause of the retrograde course and descent of the fluid in the proper vessels. Nor can any supposed elasticity of the fibres of plants account for the spontaneous movements of their leaves and flowers, or of these motions which they perform when excited by external impressions. The similarity of these actions and motions in the vegetable system, to those performed in the animal system, for the attainment of similar ends, sufficiently warrants the conclusion, that they originate in a similar cause, or arise from that peculiar property, irritability, or the susceptibility of contraction from the application of external agents, which characterizes living animal matter.

From the structure of vegetables, and in particular the greater rigidity of their parts, the immediate operation of this principle is not indeed so unequivocally perceived. But the functions of the vegetable kingdom;—the absorption of external matter; the propulsion of the sap; the secretions whence new products are formed; the motions of their leaves; their susceptibility to the impression of external agents, light, heat, moisture, and electricity; their growth, and the formation and evolution of the embryo plant with similar powers, are phenomena inexplicable on any principles of mechanism, and so strikingly analogous to the phenomena which occur in the animal system, that they must be referred to a similar principle.

The irritability of vegetables, observes, even in its relations to external agents, nearly the same laws as animal irritability. The functions dependent on it, require to be excited by the application of external agents: hence the necessity of the due application of heat, light, air, and moisture: if these are withdrawn, the functions languish, and the irritability of the plant accumulates; if they are applied in excess, this power is impaired; and, lastly, if by a previous abstraction of the usual stimuli, the irritability has been accumulated, more vigorous action will ensue on their re-application, or, if too suddenly and forcibly applied, a total exhaustion of power will take place. The effects of soil, of moisture, of heat, light, and electricity on plants; their sleep, germination, efflorescence, fructification and decay, afford many beautiful illustrations of the operation of this principle, in conformity to these laws.

It is true, that some differences are to be observed in the vitality of the two systems. They are differently acted on by some agents, and there does not exist in the vegetable system, at least to so great a degree as in the animal system, that general relation, by which, when one part is peculiarly affected, distant parts participate in the affection. But differences of this kind are comparatively trivial: they arise from a more simple structure, and they are not greater than what are even to be observed in the different orders of animals.

The preceding observations on the structure and moving powers of vegetables, and on the circulation of their fluids, prepare us for the consideration of the functions on which their growth is dependent, and by which, from new combinations, their various products are formed.

Absorption takes place in vegetables to a very considerable extent. A large quantity of water, with portions of other matter, is taken up by their roots from the soil, and is indispensable to their growth. This absorption is not indiscriminate, otherwise plants should contain all the principles of the soil in which they grow. Neither is it pure water only that is absorbed, but water holding in solution or in suspension such substances as may contribute to the nourishment of the plant. The absorption of this fluid, is the source of the sap or common juice, which rises through the vessels in the alburnum, is gradually changed in its progress through the plant, and which is found in very different states at different periods. In winter it is in small quantity; in spring and summer it is much more abundant; in autumn it becomes thicker and less copious;—changes which may arise partly from the action of the sap vessels, partly from intermixture of the proper juices, or from the solution of part of the solid matter through which it is conveyed. Dr Darwin observed, that the qualities of the sap, in certain periods of vegetation, appear in particular to arise from the matter which it dissolves in its ascent. He supposed, that when vegetation is vigorous, as it is in the course of the summer and commencement of autumn, a quantity of nutritious matter is formed principally by the leaves, and is deposited as a reservoir of nutriment in the alburnum; that on the revival of vegetation in the spring, this is dissolved by the fluid which is then absorbed from the soil, communicates to it peculiar qualities, and serves for the formation of new buds and leaves. In herbaceous plants, this deposition, he observes, takes place in their roots during the autumn for the same purpose; and in some plants it is formed in the joints of the stem. Hence, as he remarks, the leaves of the lower branches of trees are usually first expanded *.

Mr Knight has stated precisely the same view,—that part of the proper juice generated in the plant when vegetation is most vigorous, that is, in the course of the summer and the commencement of autumn, is deposited

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* Phytologia, p. 28. 32. 168. 163.

in the solid matter of the alburnum, and remains deposited in it through the winter. In the spring, when the powers of vegetation are renewed, this deposite is supposed to be dissolved by the ascending sap, and thus matter is furnished already assimilated to the vegetable, and adapted to the formation of the new buds and shoots. In conformity to this opinion, and what may be regarded in some measure as proofs of it, Mr Knight found, that the sap in spring has a greater specific gravity, and possesses qualities which indicate a quantity of some peculiar matter to be dissolved in it, in a greater degree, as it is taken at a greater height from the root; and that the wood of the stem or large branches, cut down in winter, has a greater specific gravity, and contains more extractive matter soluble in water, than the wood of the same species of tree cut down about the commencement of summer *.

It appears also, that in other periods of vegetation, the sap is mingled with some of the proper juices, as it is sometimes possessed of qualities which it could not have derived from the soil, or from any of the solid parts of the plant. It is thus sometimes highly saccharine, though the wood itself is possessed of no sweetness; at other times acid. According to Mr Knight's observations, the sap, whether extracted from the tree nigh to the ground, or at a distance from it, was always found to contain a large portion of air.

The sap of different vegetables has been examined by Vauquelin. The sap of the common elm, (Ulmus cam-

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* Philosophical Transactions, 1805, p. 70. 101.

pestris), he found to contain a large portion of vegetable matter, acetate of potassa, carbonate of lime, with slight traces of sulphate and muriate of potassa, the vegetable matter being in larger proportion, as it was taken from the plant late in the season. The sap of the beech, (Fagus sylvestris), besides vegetable extractive matter, contained tannin, gallic acid, and free acetic acid, without any carbonate of lime, but with a portion of acetate of lime. The sap of the birch with extractive, contained also saccharine matter, acetic acid, acetate of lime, and nitrate of potassa. In all these saps, part of the proper juices had no doubt been mixed with the liquid absorbed from the soil, or part of the solid vegetable matter itself had been dissolved in its progress through the plant *. Chaptal has also examined the sap of various vegetables, obtained by exudation from incisions, and probably in a state of mixture with the proper juices. In all of them a quantity of vegetable extractive matter was contained, having principally the characters of the matter which constitutes the ligneous fibre, which was slowly precipitated on standing either with or without the admission of the air, and which was also precipitated by acids, alkalis, and other re-agents †.

Not only is absorption performed by the vessels in the roots of plants; it takes place also at the surface of the bark and leaves. Absorbent vessels are not only capable of being discovered by the eye, running from the bark in a horizontal direction, but the performance of absorption

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* Annales de Chimie, tom. xxxi. p. 20.

† Mémoires de l'Institut. National, tom. i. p. 288.

by them is demonstrated, by the increase of weight which a branch taken from a tree gains by exposure to dew, or to a humid atmosphere. The absorbents from the leaves seem to rise principally from the inferior surface of the leaf.

Perspiration, or the function by which a fluid or vapour is constantly exhaled, is that which counterbalances Absorption. Numerous experiments have proved the existence of this function in vegetables. By merely placing a growing plant under a glass receiver, the internal surface is soon obscured; a fluid is condensed on it, which appears to be water, with a slightly odorous impregnation. The quantity perspired differs under various circumstances. It is increased by a high temperature, by the stimulus of light, and by a dry atmosphere. In the experiments of Hales, a sunflower, three feet high, was found to transmit by transpiration, in twelve hours in the daytime, about twenty ounces of fluid. This function appears to be performed by the leaves, and principally by their under surface, as has been already stated. There also exist, however, numerous pores or apertures in the bark of the stem and branches, through which, probably, a discharge of fluid likewise takes place.

Respiration is another function which plants have been supposed to perform; and there can be no doubt, but that they are affected by, and produce changes in the surrounding atmosphere, and in aerial fluids, to the action of which they are exposed. The nature of these changes, however, though the investigation of it has been the subject of very numerous and extensive experiments, is still involved in some obscurity; and the statement of this function, so important in what relates to the chemical physiology of vegetables, will require some details.

At an early period of pneumatic chemistry, (1771, or 1772), Priestley, from some facts which he had observed, inferred, that plants growing in air vitiated by combustion or the respiration of animals restore it to its original purity. A few years afterwards, he undertook the more full investigation of this subject; and though in the course of his experiments, the results were variable, and sometimes discordant, he found, that in many of them, when a plant, or the shoot of a plant, was introduced and confined in air which had been vitiated by respiration or the combustion of a taper, in which, of course, carbonic acid was present, while the oxygen was nearly or entirely abstracted, in a few days the air was found to have received an accession of oxygen gas, so as to suffer a diminution of volume from the addition of nitrous oxide gas, which it previously did not do; and, in some cases, the proportion of oxygen appears to have been increased to even more than the usual proportion in atmospheric air*. And, in other experiments made at a later period, he found, that air containing a large proportion of oxygen was evolved from aquatic plants immersed in water, and exposed to the solar light †.

This office, apparently performed by the vegetable kingdom, opened an admirable view of adjustment in the economy of nature. All the tribes of animals consume, in respiration, part of the oxygen of the air which they breathe, and form, at the same time, a portion of carbonic acid gas, which they expire; and the necessary effect of both these operations is to deteriorate the atmosphere, or render it less fit to support life. It may be concluded, therefore, that there are causes equally constant and general in their action by which these are counteracted, and the purity of the atmosphere preserved. This was supposed to be performed by the vegetable kingdom. The experiments of Dr Priestley were regarded as proving, that growing plants give oxygen to the atmosphere; and other experiments seemed likewise to prove, that they absorb and decompose carbonic acid. The one tribe of animated beings, therefore, appear opposed to the other in the changes they induce on the air which is indispensable to both; and, by these reciprocal changes, it is preserved in a state adapted to the support of each.

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* Experiments on Air, vol. iv. sect. 28.

† Ibid. vol. v. sect 2.

I have stated, however, that the results of Dr Priestley's experiments were by no means uniform, and, in many of them, the changes produced by vegetation in the air appeared to be precisely the reverse. He frequently found, that the air vitiated by combustion or respiration, to which the plant was exposed, was not ameliorated, without being able always to discover the reason why it was not: sometimes the air was even farther injured, and in other experiments he found, that common air was diminished, and rendered noxious *. In the experiments made nearly at the same time, too, by Scheele, the purity of the air was always injured both by germination and vegetation. Pease were confined in a matrass, over wa-

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* Experiments on Air, vol. iv. p. 299. 301. 321.

ter, in which they soon struck out roots and grew; and when they had ceased growing, the air, on being examined, was found to have remained nearly the same in volume, but its oxygen was consumed, and a quantity of carbonic acid gas, equal to the oxygen in volume, had been formed. Scheele adds to the account of this experiment, that he had "preserved fresh roots, fruits, herbs, flowers, and leaves, each separately in a matrass, and found, after some days, one-fourth of the air changed into aërial acid," or carbonic acid gas *.

On the other hand, the conclusions of Priestley appeared to receive confirmation, to a certain extent at least, from a series of experiments by Ingenhousz. Priestley himself had observed, that when water is kept for some time in glass vessels, and particularly, when any vegetable had been previously immersed in it, a quantity of a green matter is generated, which he considered to be of a vegetable nature †. This matter, he found, when exposed in water to the solar light, gave out a considerable quantity of an aëriform fluid, nearly pure oxygen gas; and a similar production of this gas he found to take place from aquatic plants, exposed under water to the action of light ‡. Ingenhousz prosecuted this investigation to a greater extent. He found, that not only from the green matter of Priestley, but likewise from the leaves of vegetables, from their green branches or shoots, or even from the entire vegetable, when placed under water and exposed to the solar light, oxygen gas, in a state generally of considerable purity, is evolved *; and, as the result of his numerous experiments, he adopted the conclusion, that oxygen is elaborated in the leaves or other organs of vegetables, by a vital action excited and sustained by the solar light †. That the organic structure of the leaf is necessary to this production of oxygen, and that it is therefore the result of a function performed by it, Ingenhousz supposed to be proved by the facts, that after a short time, (about two days in general), the emission of oxygen ceased, in consequence, as he supposed, of the vessels of the leaf gradually losing their vital powers; and that leaves which had been bruised gave out no oxygen, while the leaves of the same plant detached from it, but without this destruction of their organization, gave oxygen, the other circumstances being precisely the same. At the same time, he likewise found, that when the light is excluded, not only does the evolution of oxygen cease, but the plant, if placed either in atmospheric air or in oxygen gas, consumes oxygen and produces carbonic acid, and the general result of all his experiments is, as he announces it, that vegetables always deteriorate the atmosphere, except when exposed directly to the solar light ‡.

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* Experiments on Air and Fire, p. 150.

† Others, particularly Ingenhousz, have considered this green matter as a collection of animalculæ.

‡ Experiments on Air, vol. iv. p. 335.; vol. v. p. 16. 23. 32.

The experiments of Priestley and Ingenhousz, proving the evolution of oxygen gas from vegetables, were always

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* Experiences sur les Vegetaux, tom. i. p. 22 25. 105. 230. 231, &c.

† Ibid. tom. i. p. 43. 91.

‡ Ibid. p. 61. 251.; tom. ii. p. 49. 102.

liable, however, from the manner in which they were made, to the objection, that the oxygen evolved might be the product, not of the process of vegetation, but of the action of the solar light on the water; the vegetable matter affording merely a surface, which presented the water in a favourable manner to the action of the light; that the oxygen, therefore, might be derived entirely from the water, being either the portion which water always holds dissolved, or part even of the oxygen which enters into the composition of that fluid. With this supposition, the fact ascertained by Ingenhousz, that when the light is not present, vegetables consume the oxygen of the air, and form carbonic acid, sufficiently accords; for it appears improbable, that vegetables should perform such opposite functions, as at one time to produce oxygen, at another to consume it; or that they should be so much dependent on an external agent, constantly variable, as that, by its application, they should perform one function, and, on its abstraction, not only cease performing this, but perform one precisely the reverse. It might rather be concluded, that the function which they do perform when the light is excluded, is that which is natural to them; and that the ceasing of this, when they are immersed under water and exposed to the solar light, is owing to the exclusion of the atmospheric air; while the evolution of oxygen, which under these circumstances also takes place, may be owing merely to the chemical action of the light on the water. Other facts agree with these conclusions. If the evolution of oxygen depended on the action of the light on the water, it might be concluded, that it would vary somewhat, according to the nature of the water, as, for example, whether it held more or less air in solution; while, if it were the result of the process of vegetation, or of any function performed by the vegetable, it could be little affected by such a cause. And it equally follows, that, were the oxygen evolved from the plant, the evolution ought to continue as long as it continued to perform its functions; while, if it were derived from the air dissolved by the water, the evolution must soon cease. Now, on these points, the facts observed both by Ingenhousz and Priestley are at variance with the conclusion, that the oxygen is emitted by the vegetable. They both observed, that the emission was materially dependent on the kind of water in which the vegetable matter was immersed. It was more abundant from water drawn by a pump than from any other; more so from river-water than from rain-water, and less copious, as well as less pure, from stagnant water, or water that had been boiled, or distilled *. The evolution, also, in the same quantity of water, continued only for a limited time, and that this could not, as Ingenhousz imagined, arise from the termination of the life or functions of the vegetable, supposing the evolution to have arisen from that cause, was apparent from the fact likewise observed by Priestley †, that, on removing the water, and adding a new quantity, the production of oxygen took place as before. These facts, it must be acknowledged, appear to

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* Priestley's Experiments on Air, vol. v. p. 35. 36. Ingenhousz Expériences sur les Végétaux, tom. i. p. 282.

† Experiments on Air, vol. v. p. 25.

establish the conclusion, that the production of oxygen from vegetable matter, under the circumstances observed by Priestley and Ingenhousz, is not the result of any function of the living vegetable, but rather of the chemical action of the light on the water, or, at farthest, on the humid vegetable matter.

Yet these objections, though they appear at first to have some force, have perhaps been obviated, or at least more than balanced, by the numerous facts which Priestley's and Ingenhousz's experiments establish. It does not follow, as has been contended, that although in the shade plants *may consume* oxygen, and *form* carbonic acid, the same functions *must* be performed when light is introduced; since *this* principle may both change the exertion of the vital agencies of the plant, and exert chemical affinities that may materially modify the results; nor can an argument thus drawn merely from reasoning be opposed to an actual experiment. That the leaf does not operate merely by affording a surface, at which the light acts in a favourable manner on the water, Ingenhousz appears to have established in a very satisfactory manner; as well even as the farther deduction, that the leaf operates in these experiments in consequence of its organic structure, and the actions connected with this. Thus, in exposing to the solar light, in separate portions of the same water, living vegetables, or the leaf of a plant newly detached, and substances which might equally afford a surface on which the light might act, as pieces of silk or cloth, while the former afforded very pure oxygen, the latter gave none *: the oxygen given out is purer when the upper surface than when the under surface of the leaf is exposed to the light [*]: and a larger quantity of oxygen is given out from leaves in a state of maturity and vigour, than from those which are feeble, and imperfectly developed [†]. While the leaves thus give oxygen, and improve the air, the flowers and other parts of the plant always deteriorate it [‡]: leaves which are dead, or have their organization destroyed, give out no oxygen [||]: the emission of this gas from leaves under exposure to light, in conformity to this last fact, continues only for a certain time: and, lastly, the quantity of oxygen evolved is greater than can be supposed to be derived from the air which water holds in solution; and the water surrounding the leaf, when the cessation of the production of oxygen has taken place, instead of being deprived, is, as Ingenhousz has remarked [¶], saturated with it, sparkles when agitated, and gives it out when exposed to heat. All these facts appear to prove, that the production of the oxygen, under these circumstances, is the result of a function performed by the living leaf, and capable of being performed by it alone.

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* Philosophical Transactions, vol. lxxii. p. 426.

Independent of this proof, the facts which have been stated in opposition to this conclusion are sufficiently reconciled with it, if a discovery announced by Sennebier, and confirmed by Woodhouse and Saussure, be regarded as sufficiently established,—that the production of oxygen by plants, exposed in connection with water to the solar light, depends principally on the carbonic acid which the water contains. Sennebier remarked, that, according to the experiments of Priestley and Ingenhousz, the leaves of plants exposed to light in water which had been boiled, gave no oxygen gas, a fact which he verified by experiment; while, when placed in well-water newly drawn, this gas was emitted.' The object, then, was to discover, what circumstance attending the well-water favoured this production of oxygen; and this, Sennebier supposed, was a portion of carbonic acid contained in this water, the decomposition of which afforded the oxygen. He therefore impregnated water with carbonic acid, in different proportions, and compared the quantity of air given out, when leaves were expoſed to the solar light in theſe portions of water and in common water, or water which had been boiled. In the last, he found no air to be given out; in the common water, a little was evolved; and a much larger quantity was emitted from the water impregnated with carbonic acid. He farther found, that, after a certain time, the impregnated water lost this superiority, and that it lost it instantly when the carbonic acid was abstracted by boiling, or by the addition of lime-water; while, if a little acid was added, to disengage the carbonic acid from the lime, the power of furnishing oxygen was restored. These facts appear to prove, that the production of oxygen, when leaves are exposed immersed in water to the solar light, depends, if not entirely, at least in a great measure, on the decomposition of the carbonic acid contained in the water *

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[*] Experiences sur les Vegetaux, tom. ii. p. 193.

[†] Ibid. tom. i. p. 108. 316.

[‡] Ibid. p. 67. 71. 269. 274.

[||] Ibid. p. 127.

[¶] Philosoph. Trans. vol. lxxii. p 4[illegible]1.

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* Journal de Physique, tom. xli. p. 206.
Physiologie Vegetal. tom. iii. p. 198.

These experiments have been confirmed by other authorities. Ingenhousz found, that if vegetables are submitted to the action of the solar light, under water which has been boiled strongly, no oxygen gas is obtained; but, on impregnating this water with carbonic acid, oxygen is obtained in large quantity, and of great purity *. Woodhouse found, that the air produced by the exposure of the leaves of plants to the solar light in river water, was principally nitrogen; while that from the same water, with carbonic acid, was oxygen gas, of a high degree of purity. "The leaves of thirteen different plants, separately exposed in forty ounce measures of the water of the river Schuylkill, produced about ten drachm measures of air, the principal part of which was azotic gas; whereas the same kind of leaves, exposed in the same quantity of the same water, impregnated with carbonic acid, yielded seventy-seven drachm measures of oxigenous air, of a very high degree of purity †." It is to be observed, however, that when the water is too strongly impregnated with the carbonic acid, it proves injurious to plants. This was ascertained both by Priestley and Ingenhousz. It is only when it is more slightly impregnated, as Ingenhousz has remarked, that they flourish, and that oxygen is evolved ‡.

There is another cause, too, which has been assigned by Ingenhousz, why the kind of water employed in the experiment appears to influence the production of oxygen.

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* Experiences sur les Vegetaux, tom. ii. p. 78.

† Nicholson's Journal, 8vo. vol. ii. p. 157.

‡ Experiences sur les Vegetaux, tom. i. p. 290.; tom. ii. p. 282. 296. 408.

In water that has been boiled, the air it held in solution is expelled; and hence, when oxygen is emitted by the leaf exposed to the solar light in such water, the first portions are absorbed by the water, and it does not pass to the elastic state until the water is saturated, while, in common water, there is no loss from this cause *.

A series of experiments made some years ago by Count Rumford, has been supposed to afford results unfavourable to the conclusion, that the production of oxygen depends on a function performed by the leaf, and connected with its organization and life. In these experiments, various inorganic substances, such as raw silk, eider down, cotton, and linen, immersed in water, and exposed to the solar light, gave out oxygen gas, some of them in as large quantity and in as great purity as vegetables do †. Though considerable stress has been laid on these experiments, they are, however, little conclusive. In almost all of them, the experiment was continued several days before the air produced was withdrawn and examined; and Ingenhousz, in some observations on them ‡, very justly remarked, that the production of the oxygen might be from the green matter originally observed by Priestley, which is always generated when water is exposed to light with any vegetable or animal matter. Rumford himself, in relating his experiments, generally states, that the water lost somewhat of its transparency, and acquired a greenish tinge ‖;

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* Philosophical Transactions, vol. lxxii. p. 429.

† Ibid. 1787, p 84.

‡ Experiences sur les Vegétaux, tom ii. p. 362.

‖ Philosoph. Tran. 1787, p. 87. 96, 97. 100. 102. 106.

and he adds, that, on examining water which had acquired this green tinge, he found, that the green matter, which, with Ingenhousz, he considers as a collection of animalculæ, had been formed *. In some of the experiments, the evolution of air took place sooner than it could be supposed any matter of this kind was generated, but, in the experiments in which the air evolved at this early period was examined, it was found, with the exception, in one or two experiments, of the air from raw silk, to be not oxygen, but apparently nitrogen, or, to use the term in which the fact was expressed, "was much worse than common air;" and it was only after the fifth or sixth day, when the production of the green matter might have taken place, that the production of oxygen commenced †; and, in one of the experiments, the appearance of the green matter, at the time when the oxygen began to be produced, is distinctly remarked: on the fifth day, "the water changing suddenly to a greenish colour, began all at once to give good air in great abundance" He observed also ‡, that the leaves of vegetables lost their power of emitting oxygen, when exposed in water to the solar light, after an exposure of two or three days, (the organization and life of the leaf being probably by this time subverted): they then, for a certain interval of time, furnish no oxygen,—a fact directly subversive of the opinion, that any dead inorganic matter, immersed in water and exposed to light, will afford air, in consequence of afford-

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* Philosophical Transactions, 1787, p. 111.

† Ibid. p. 103. 105. 108.

‡ Ibid. p. 119.

ing a surface at which the light can act on the water. But after this interval, they again resumed the power of affording oxygen; the peculiar green matter which affords that principle being then produced,—a fact which strongly proves its agency in all these experiments. And, lastly, Rumford found, that in employing a substance which could neither exert any chemical agency on the water, nor contribute to the production of the peculiar green matter, but merely afford a surface, whence the air contained in the water might be extricated by the agency of light,—such, for example, as fine spun glass; in this case, very little air was extracted, and the small quantity obtained, instead of being oxygen, was rather worse than common air, and, as Rumford remarked, "was doubtless merely the air with which the water had been overcharged *." These experiments, therefore, rather confirm than invalidate those of Priestley and Ingenhousz.

Experiments performed by immersing the plant in water may still, however, be supposed liable to some sources of fallacy; and it must be considered as more satisfactory, to determine the changes occasioned in the surrounding air by a vegetable in its natural situation. This has accordingly been repeatedly made the subject of experiment, but with results far from being uniform.

Dr Priestley, at an early period of his researches, had observed, as has been stated, that air injured by respiration, putrefaction, or combustion, was meliorated by plants growing in it, though sometimes it was rather farther injured †.

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* Philosophical Transactions, 1787, p. 113.

† Experiments on Air, vol. 1, p. 91.

In the latter case, however, it appears from his experiments, that the plant confined in the air was growing in earth; and the action of the vegetable mould might have given rise to the result he observed. In other cases, where he merely introduced the flexible shoots of plants, by bending them, into jars of air, the air was ameliorated; and he observes, that all the cases in which common air was improved by vegetation, were those in which the experiment was performed in this manner [*], of which he gives a number of examples, with regard to different plants. He found, too, that plants did not flourish when their branches were introduced into pure oxygen gas, that this also was the case when they were confined in carbonic acid gas, either pure or mixed with a portion of atmospheric air. Dr Percival, on the other hand, had observed, that carbonic acid gas, supplied to growing vegetables in a small proportion, was favourable to their growth [†]. And Mr Henry *senior*, in repeating these experiments, had observed the same result; observing, at the same time, that, when the vegetables submitted to experiment were confined in pure carbonic acid gas, they soon died [‡]. Ingenhousz had remarked, that plants, confined in an atmosphere containing a portion of carbonic gas, decompose it, or convert it into oxygen gas, when exposed to the solar light; and he stated, at the same time, that the *direct* application of this light is necessary; so that, when it is even only partially excluded, the conversion does not take place, and, in a dark place, oxygen is consumed, and converted into carbonic acid *. He farther observed, that air vitiated by respiration is restored to its former purity, by shoots or branches of various plants being confined in bottles filled with it, and exposed to the solar light; and this happens without the presence of water: "A leaf of a vine, inclosed in a flask capable of containing about an ounce of water full of air infected by respiration, will re-establish it in an hour and a half †." The experiments of Sennebier nearly correspond with those of Priestley. He found, that the air inclosed with the branches of plants under glass receivers, placed over water, and exposed to the sun, was almost always a little ameliorated; and was still more so, when the branches were removed during the night, and when they were renewed every day, or were in connection with the plant. He found also, that when branches were exposed to the light in this manner in nitrogen or hydrogen gas, renewing them every day, and observing the result daily, there was progressively an addition of oxygen gas, so that, at length, a taper introduced into the nitrogen gas burned brightly, and the hydrogen gas, on transmitting through it the electric spark, gave a violent detonation ‡.

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[*] Experiments on Air, vol. iv. p. 300. 305. 307.

[†] Manchester Memoirs, vol. ii. p. 346.

[‡] Ibid. p. 357.

This subject has been still more lately investigated, and several series of experiments performed, but with results which are still more discordant.

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* Experiences sur les Vegetaux, tom. i. p. 52. 263

† Journal de Physique, tom. xxviii. p. 84. 88.

‡ Physiologie Vegetale, tom. iii. p. 2

The first of these have been performed by Dr Woodhouse, professor of chemistry at Philadelphia. He confined various plants in atmospheric air, exposing them at the same time to the solar light. "Carbonic acid gas was generally formed; and whenever this circumstance happened, the purity of the air was diminished." The results were similar when they were confined in oxygen gas, the plant, however, generally soon dying in this situation. Dr Woodhouse, however, instead of inferring from his experiments that the consumption of oxygen and formation of carbonic acid were functions performed by the living plant, rather concluded, that the production of the carbonic acid is from the leaves of the confined plant in part decaying, and the oxygen of the air uniting with the carbonaceous matter of the dead portion of the leaf. He supposed even, that the carbonic acid is decomposed by the living leaf, its carbon abstracted, and the oxygen evolved. And in confirmation of this opinion he states the experiment, that when leaves of different plants were exposed to the solar light in atmospheric air, having a quantity of carbonic acid mixed with it, the carbonic acid disappeared, and the atmospheric air was much increased in purity. He found also, that leaves immersed in water containing carbonic acid, afforded oxygen on exposure to solar light; while, if the water contained no carbonic acid, they afforded an air which was principally nitrogen. Hence he concludes, that in all cases where oxygen appears to be produced by vegetables, it is derived from the decomposition of carbonic acid; and as little of this gas is contained in the atmosphere, he supposes that the vegetable kingdom can have little effect in preserving the purity of atmospheric air. The production of carbonic acid, on the other hand, he regards as always arising from the action of the oxygen of the air on the carbon of the dead or decayed vegetable or of the soil. And with regard to the general action of vegetables on atmospheric air, he remarks, that "when a plant in perfect health, growing in a soil which contains little vegetable or animal matter, is confined in atmospherical air, it will live a long time without producing any change in it. Many of the vegetables which were the subjects of these experiments, did not affect the air in five days; some diminished its purity in three hours, and others altered it in a most slow and gradual manner, causing little change in it in twenty days *."

Theodore de Saussure appears to have formed an opinion similar to that which had been adopted by Woodhouse,—that carbonic acid is decomposed by growing vegetables: he considered this decomposition as the result of the process of vegetation; as the source of the carbon of the plant, and of the oxygen it evolves. Hence his experiments, in his extensive investigation of this subject †, were principally directed to establish the facts with regard to it; and in nearly all of them plants were exposed not to pure atmospheric air, but to this air, with a greater or less admixture of carbonic acid gas. His experiments were made by placing the plants on which he operated, after they had attained a certain height, in a vessel, in the bottom of which was such a quantity of

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* Nicholson's Journal, 8vo. vol. ii. p. 150.

† Recherchés Chemiques sur la Vegetation.

water, that the roots were immersed in it. There wer then introduced mixtures in various proportions of atmospheric air and carbonic acid gas: and the vessel were either exposed to the solar rays or placed in th shade, according to the object of the experiment When the proportion of this gas did not exceed a twelft part of the atmospheric air, it proved, according to Saussure, favourable to the progress of vegetation, or th plant flourished more than in common air: when it exceeded this much, it was prejudicial; and in an air consisting of half of its volume of carbonic acid gas, th plants perished in seven days. At the same time, oxyge must likewise be present to admit of the plant receivin benefit from the admixture of carbonic acid gas. In th atmosphere, of which carbonic acid forms a part, and i which the plant vegetates when exposed to light, th carbonic acid is, according to this chemist, always consumed; its carbon enters into the composition of the vegetable matter, and part of its oxygen is expended in th same manner, while the remaining oxygen, with a smal and variable proportion of nitrogen, are exhaled.

Thus seven plants of the *Vinca minor* having been introduced into a mixture of atmospheric air and carboni acid gas, (the latter amounting to 7½ parts in 100), wer confined over mercury, on the surface of which was a little water, the roots of the plants being in a separate vessel, and under these arrangements were exposed six successive days to the direct rays of the sun. On th seventh day the air had suffered no alteration in volume; but in its composition it was entirely changed: lim water gave no indication of any carbonic acid in it, whil the phosphorus eudiometer indicated the proportion of oxygen to be $\frac{21\frac{1}{2}}{100}$; the original proportion, as determined by the phosphorus, being $\frac{21}{100}$. Or the following table, present the results more distinctly:

The original air employed in the experiment, contained of

Nitrogen gas 211.92 cubic inches, oxygen 56.33, carbonic acid 21.75.

The air, at the termination of the experiment, contained of

Nitrogen gas 218.95 cubic inches, of oxygen 71.05, of carbonic acid 0.

Hence 21¾ cubic inches of carbonic acid gas had been consumed by the vegetables: if the oxygen of this had been all emitted, it would have occupied a volume about equal to that of the carbonic acid which had disappeared; but the quantity added amounted only to 14¾ cubic inches; hence 7 cubic inches, or about the half of that exhaled, is retained by the plant and assimilated, while a portion of nitrogen gas (7 cubic inches) had been exhaled by it.

From a comparative experiment, Saussure adds, he found that the seven plants of the Vinca minor which he employed, would have furnished, by decomposition in close vessels, 9.95 grains of charcoal, previous to exposure to the atmosphere containing carbonic acid gas; while the same plants, after that exposure, afforded of charcoal 12.23 grains. These results, both as to the consumption of carbonic acid, evolution of oxygen, and increase of carbon in the plant, were confirmed by a number of experiments on other plants, (Mentha aquatica, Lythrium salicaria, Pinus genevensis, Cactus opuntia), and the general conclusion established, that under exposure to light, plants always decompose carbonic acid by their leaves, retain its carbon and part of its oxygen, while the remaining oxygen with a portion of nitrogen are exhaled *.

It is this decomposition of carbonic acid which, according to the views of Saussure, is the source of the carbon in plants; since, when made to vegetate in pure water and in an atmosphere deprived of carbonic acid, he found, that they increased in bulk only, without acquiring any addition of carbon, or with even a slight diminution of it. But in common atmospheric air, where a small portion of carbonic acid is constantly supplied to them, amounting, according to his estimate, to $\frac{1}{500}$ of the air, he has found, (in opposition to Hassenfratz, who had stated from some experiments †, that plants vegetating in pure water, and in atmospheric air, contain, after their growth is established, even a less quantity of carbon than before), that the proportion of carbon is augmented, undoubtedly from this source. Thus the roots of the Mentha piperita being plunged in bottles full of distilled water, and allowed to vegetate, under exposure to the air and light, it was ascertained by comparative experiments, that 100 parts by weight of the plants employed, contained 40.29 of dry vegetable matter, which afforded 10.96 of carbon; while after vegetating, as in the above experiment,

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* Recherches, p. 42, 43.

† Annales de Chimie, tom. xiii.

for 2½ months, the 100 parts had increased in weight to 216 parts, which dried weighed 62; and from these were obtained, by decomposition in close vessels, 15.78 of charcoal, or 4.82 more than what they contained at the commencement of the experiment. A similar result was obtained, when beans were made to vegetate in pieces of flint, in a glass capsule, and supplied with distilled water. The original beans gave 22¼ grains of charcoal; while after vegetation in the open air for three months, the plants afforded 51 grains *.

When light is not applied to plants, other actions are exerted. Carbonic acid, instead of promoting the vegetation, is hurtful to it, and does not appear to be decomposed, or is decomposed at least only in minute quantity. In atmospheric air freed from carbonic acid, the recent leaves, when light is not present, consume a portion of the oxygen, and after a short time, or some of them immediately, form carbonic acid gas which is expired †. This, if not removed, proves injurious, while the plant remains in obscurity. But if light be admitted, it is then rather advantageous, the plant again decomposes it, retains its carbon, and emits its oxygen. Thus, if the vegetable, under exposure to light, be inclosed in atmospheric air with a portion of lime or a solution of potassa, which absorbs any carbonic acid that has been formed under the previous abstraction of light, it soon dies, the leaves falling entirely from the branches in five or six days. If kept in the shade, however, the lime or alkali, instead of being hurtful to vegetation, is rather favourable, as it removes

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* Recherches, p. 50. 52.

† Ibid. p. 64. &c.

the carbonic acid gas, which the vegetable, without the assistance of light, is unable to decompose *.

These functions are performed by the green parts of plants, principally by the leaves. The root, wood, and even the petals of the plant, yield only carbon to the oxygen which surrounds them.

The summary view, therefore, of the function of respiration performed by vegetables, and its connection with their growth, as given by T. Saussure, is, that plants under exposure to light, absorb and decompose carbonic acid, whether supplied by the atmosphere, by water, or from the soil; its carbon, with part of its oxygen, enter into their composition, and the remaining oxygen is exhaled. In darkness this oxygen, or the oxygen of the surrounding air, is again consumed or absorbed; it acts on the matter of the plant, combines with its carbon, and again forms carbonic acid, which is exhaled: on the return of light, this is decomposed, its carbon and part of its oxygen transferred to the plant, and its remaining oxygen exhaled; and hence, if a plant be exposed alter-

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* Saussure has remarked, that these effects by the lime or alkali, are not produced on thick-leaved plants, as the Cactus opuntia, owing, as he supposes, to the parenchyma of the leaf being so thick, and the epidermis so close, that they retain more strongly the carbonic acid. If lime only had been used, we might have been led to suspect that its operation might be owing, as Mr Ellis has since suggested, to its depriving the leaf of humidity; but the same operation being exerted by the alkaline solution, appears to preclude this objection. Saussure had also before remarked, that the operation of the lime is the same when it is previously moistened with water †.

† Annales de Chimie, tom xxiv p 128

nately to the light and shade, neither the volume nor purity of the air is altered. It is only by submitting to separate examination the effects in the shade, and under exposure to light, that these are discovered, and the preceding results can be established *.

A series of experiments has been lately published by Mr Ellis †, which present a different and more simple view of the effects of vegetation on atmospheric air, and of the share which it has in that process. They lead to the important conclusion, not before, I believe, distinctly advanced by any of those who have investigated this subject,—that the function of respiration is, as to its results, the same in vegetables as in animals; that the former as well as the latter, in all situations, consume the oxygen of the air, by converting it into carbonic acid.

It had been sufficiently established by the experiments of Scheele, Ingenhousz, Gough, Cruickshank, and others, that, during the process of germination, oxygen is consumed and carbonic acid formed. But it had been always imagined, that when the germination is completed, and the structure and powers of the plant developed, this ceases, and other functions commence, giving rise to very different results. With regard to the changes effected in the surrounding air, according to the experiments of Mr Ellis, the same process is still continued; and in vegetation as well as in germination, oxygen is consumed and carbonic acid formed.

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* Recherches, p. 91.

† Inquiry into the changes induced on Atmospheric Air by the Germination of Seeds, the Vegetation of Plants, and the Respiration of Animals.

He placed some seeds of mustard, which had been brought to vegetate on moistened flannel, and had grown to the height of more than an inch, in a jar of atmospheric air, supporting them by a small whalebone hoop covered with netting. A quantity of lime-water in a glass was placed beneath the hoop, and the mouth of the inverted jar was surrounded with water. In a few hours a thick pellicle overspread the lime-water: at the end of twenty-four hours it was very turbid, and the water had risen half an inch within the jar: at the end of the third day it had risen nearly an inch within the jar: the plants now began to look sickly, gradually drooped, and by the ninth day fell down against the sides of the jar. The residual air extinguished a taper, and rendered lime-water milky, with a further diminution of volume. Its oxygen therefore had been consumed, and carbonic acid formed. The results were similar when the experiment was performed over quicksilver.

In subsequent experiments, the changes in the air were determined with still more precision, and were always found to be the same. Its oxygen was uniformly consumed and replaced by carbonic acid gas, the proportion of which was such, that there was on the whole little diminution of volume; the carbonic acid gas produced, being nearly equal in volume to the oxygen consumed. Carbonic acid gas, Mr Ellis endeavours to shew, is not necessary to the growth of plants; since the plant dies when it is abundantly supplied with it, if oxygen be not present, and, on the other hand, it lives and flourishes as long as it is supplied with oxygen, though carbonic acid be completely abstracted from it. The experiments of Saussure in which plants died when a quantity of lime was put into the jar in which they were confined, so as to abstract the carbonic acid, he explains on the supposition, that its decay was owing not to this abstraction, but rather to the abstraction of the humidity of the plant by the lime; and he found, that when the carbonic acid alone is abstracted, as by solution of potassa, the plant does not decay from this cause *. The experiments of Priestley and Ingenhousz, in proof of the emission of oxygen by the leaves of plants when immersed in water and acted on by light, he contends are inconclusive, as the leaf in this situation, and especially as detached from the plant, cannot be supposed to perform its natural function.

I have repeatedly witnessed Mr Ellis's experiments, and been fully satisfied of their accuracy, or that the results were precisely as described, and established without any apparent source of fallacy. Yet from the preceding account it must be obvious, that they are irreconcilable with the experiments of others; and although they agree with the experiments of Scheele, and in some measure with those of Woodhouse, yet the discordance with those of so many others leads to the suspicion, that there are still some circumstances having an important influence in these operations, which give rise to such differences, and which require to be ascertained. The whole subject is still involved indeed in such obscurity and uncertainty, that the most opposite facts appear to be established by different authorities.

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* This last result is however at variance with the experiments of Saussure, in which the alkaline solution is said to have had the same injurious operation on the plant as lime had.

Thus, independent of the question with regard to the production of oxygen by leaves exposed under water to the solar light, which has been already considered, there are results with regard to the nature of the changes produced by plants in the surrounding atmosphere, which appear altogether irreconcilable. That they consume oxygen and form carbonic acid, not only in the dark, (for this appears to be admitted by every experimenter), but under exposure to light, appears to be established by some of Priestley's early experiments, and by those of Scheele, as well as by those made by Mr Ellis; and that oxygen even sustains the life of vegetables, while the other gases prove fatal to them, is proved by the experiments of Ingenhousz, to be immediately stated. On the other hand, that plants consume carbonic acid, and give out oxygen gas, not only when immersed under water, in which case a source of fallacy has been supposed to exist, but even when placed in atmospheric air, or in carbonic acid gas in a state more or less diluted, is directly proved by other experiments of Priestley *, and of Ingenhousz, as well as by those of Woodhouse, Sennebier, and Saussure, already referred to. The subject is at present perhaps in that state in which we can scarcely draw a decided conclusion. Yet the weight of evidence, I must confess, appears to me still to preponderate in favour of the conclusion, that vegetables absorb and decompose carbonic acid, and give out oxygen when exposed to light; for the ex-

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* Experiments on Air, vol. i. p. 91.; vol. iv. p. 296. 300. 305, &c.

periments which establish this, are extremely numerous and diversified, and no source of fallacy has been pointed out, sufficient to account for them, supposing the fact not to be established. It is true, that there are still at variance with these, the experiments which appear to prove the consumption of oxygen, and the formation of carbonic acid; and it were desirable to discover the circumstance by which they may be reconciled. In these experiments it appears to me, that there is one source of error, which has not been sufficiently estimated, and which may even have given rise to the results that were observed. The plants submitted to experiment, both in the experiments of Scheele and of Mr Ellis, were those the white and succulent stems of which are large proportioned to their leaves; such, for example, as peas, mustard, &c. Now, it appears from the experiments of Ingenhousz and Saussure, that it is only by the green parts of plants that carbonic acid is decomposed and oxygen evolved; while from the white and succulent parts, it is established by Saussure, that carbonic acid is formed by the action of the oxygen of the surrounding air upon them; and Ingenhousz many years ago remarked, that the power of ameliorating the atmosphere, is exerted only by the leaves; that even the green shoots possess it imperfectly, and that it is not possessed by the flowers or fruit *.

An important difficulty likewise presents itself, on the supposition that plants consume oxygen, and form carbonic acid. Whence is the source of the carbon which forms this acid, as well as of that which likewise enters in-

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* Journal de Physique, tom. xxviii. p. 87.

to the composition of the vegetable matter? When they grow in a rich soil, it might be supposed that from this there will be a sufficient supply of carbon. But when they grow in water and air alone, the quantity of carbonaceous matter originally contained in the seed and root, will be found not sufficient to form the carbonic acid, which in conformity to this view they must be supposed to exhale during their growth, and still less that which enters into the composition of the vegetable itself. Nay, if we consider to how short a distance the roots of a plant extend in the soil, how little of this soil is carbonaceous matter, and how seldom, with regard to many plants, this soil requires to be renewed, it will be perceived, that though it were supposed that the carbon, which in the progress of the growth of the vegetable is fixed in its composition, were derived from the soil, it is impossible, on the supposition that plants are constantly consuming oxygen and expiring carbonic acid, to suppose, that the much larger quantity of carbon which must thus be expended in the formation of that acid, can be derived from the same source. It is true, that such a difficulty cannot be opposed to experiment, were this direct and incontrovertible; but where the experiment is otherwise, and is opposed by others, it is certain that such a difficulty must have much weight.

It is to be observed, however, in concluding this subject, that the changes effected by plants in a state of full growth and vigour, on the surrounding air, are much less than have been imagined, and that when supplied merely with water, they are so inconsiderable as not to be very perceptible. Thus Hassenfratz inclosed the branches of growing plants in atmospheric air, the roots being either in water or in earth, the surface of which was covered with a plate of tinned iron, having an aperture in it through which the stem rose, and this aperture being exactly closed with soft wax, so that a jar supported on the plate had its orifice surrounded with water. In both these modes of making the experiment he found, that though the plants grew, yet at the end of a month and a-half or two months, the air remained unaltered in volume, and in the proportion of oxygen *. It is probably principally from the soil that plants derive their nourishment, and they are unquestionably much less dependent than animals on the surrounding air. They require also a less supply of nutritious matter, as their growth is much more slow, and they lose less by any excretion.

Vegetables are capable of being acted on by the other aërial fluids, and of acting on them; though, with regard to this, considerable diversity prevails among the experiments of different chemists. According to Scheele, vegetables do not flourish in oxygen gas, but on the contrary decay and die †: and the same conclusion was drawn by Priestley from his experiments ‡. Ingenhousz, on the contrary, affirms, that a plant confined in oxygen gas, and either exposed to the light or kept in a dark place, vegetates very well, and in general lives longer and is more vigorous than when it is inclosed in a similar quantity of atmospheric air; and it lives still longer if the carbonic

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* Annales de Chimie, tom. xiii. p. 325.

† Chemical Observations and Experiments, p. 156.

‡ Experiments on Air, vol iv. p. 326.; vol. v. p. 13

acid gas which it generates, at least when kept in darkness, be abstracted, than if it be allowed to remain. The presence of oxygen gas, according to his experiments, enables it even to resist better the pernicious operation of other aërial fluids *. The results of Saussure's observations appear, on the other hand, to agree with those of Scheele and Priestley; as he found plants to flourish less when kept in the shade in pure oxygen gas, than in oxygen diluted with nitrogen or hydrogen, either from the immediate action of the oxygen or from more carbonic acid being formed †. There is some reason to believe, that in all the experiments in which oxygen has appeared injurious to vegetables, it is from this last cause that this has arisen, and that directly it is rather useful, and is even necessary to sustain the functions of plants. This in particular appears from plants dying when kept *in vacuo*, and likewise from the effects of the other gases upon them.

Priestley found, indeed, that plants grow perfectly well in nitrogen gas, or in air that had been injured by combustion or respiration ‡: but, in opposition to this, Ingenhousz affirms, that the gases which are noxious to animal life, nitrogen, hydrogen, and carbonic acid, prove injurious likewise to vegetables. When young plants are confined in any of these gases, he found them incapable of resisting their noxious operation, either in the shade or under exposure to light; and even when they have acquired

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* Experiences sur les Vegetaux, tom. ii. p. 10. 15. 21. 76.

† Recherches, p. 92.

‡ Experiments on Air, vol iv p. 30. 326

more vigour, although they resist it for a few days under favourable circumstances, they at length decay and die[*]: Carbonic acid gas appears, from his experiments, to be peculiarly injurious to vegetable life, especially if its noxious quality be not counteracted by exposure to solar light [†]. And if a plant be inclosed in common air, or in oxygen gas, and be kept in a dark place, if the carbonic acid it generates be abstracted at intervals, it grows better than if it be not removed [‡]. Priestley likewise observed, as has been already stated, that carbonic acid gas is injurious to vegetables [||]; and even Percival and Henry, who contended for its utility, admitted, that it proved hurtful if in its pure state, or unmixed with oxygen. Hydrogen gas Priestley found to be less injurious; and by some plants, as the willow, he observed it to be absorbed, without injury, in considerable quantity [¶],—an observation confirmed to a certain extent by Ingenhousz, who farther observed, that the plant, when exposed to the solar light in hydrogen gas, gives to it oxygen, so as to render it at length capable of exploding, on the approach of an ignited body [§]. According to the observations of Humboldt and others, hydrogen appears to be even capable of supplying, to a certain extent, the place of light, and of enabling plants to retain their green colour, which they otherwise lose when light is excluded *.

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[*] Experiences sur les Vegetaux, tom. ii. p. 5.

[†] Ibid. p. 72. [‡] Ibid. p. 76. 228.

[||] Experiments on Air, vol. iii. p. 303.

[¶] Ibid. vol. iv. p. 320. 330.; vol. v. p. 2.

[§] Experiences sur les Vegetaux, tom. ii. p. 330.; tom. i. p. 297.

Mr Davy some years ago observed, that some plants, minionet for example, grow in hydrogen gas, when supplied at the same time with water, absorb a portion of it, and, when exposed to light, give out oxygen; while others, as foxglove or hemlock, die in it very quickly. He observed a similar difference with regard to carbonic acid gas: many vegetables, when confined in it, and exposed to solar light, flourished, part of the carbonic acid was decomposed, and oxygen evolved; while others, especially aquatic plants, die in it in a very short time †.

Mr Gough found, that nitrogen gas is injurious to growing plants. It rather appears, however, from his experiments, to have exerted no positively noxious power, but to have proved hurtful only by excluding oxygen; as when the plant confined in it was transferred to atmospheric air, its powers of vegetation were renewed. He concludes therefore with Ingenhousz, that oxygen is necessary to sustain vegetable life ‡.

Saussure, in his late experiments, has likewise directed his attention to the influence of the different gases on vegetation. Nitrogen appeared to be incapable of sustaining it: the plant continued to grow for a short time, indeed, from the portion of oxygen which its green parts exhale; but plants not possessed of such parts, or de-

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* Journal de Physique, tom. xliii. p. 393.

† { Beddoes's Medical Contributions, p. 156. 163. 200.
{ Chemical Researches, p. 563.

‡ Nicholson's Journal, vol. ix. p. 217.

prived of them, were found not to vegetate in nitrogen. Some vegetables, in which the green parts were abundant, flourished in it for a considerable period. In darkness, plants confined in it exhaled carbonic acid. The general results, with regard to vegetation in hydrogen gas and in carbonic oxide gas, he found to be nearly the same as in nitrogen *.

The roots of vegetables perform functions with regard to aerial fluids different from the leaves. They consume oxygen, and form carbonic acid; and they are injured, and at length decay, when confined in carbonic acid, nitrogen, or hydrogen gas †. The stems and branches of plants confined in atmospheric air vitiate it either in the shade or under expoſure to light, without changing its volume, as they replace the oxygen they consume by an equal volume of carbonic acid gas. The green membranous tissue with which these parts are covered, counteracts this under exposure to light, by decomposing part of the carbonic acid which is formed; but the effect of this is very trivial ‡.

The flowers of plants produce changes on the air similar to those produced by the roots and branches. They appear to exhale also a portion of nitrogen gas in the shade ||.

Secretion is a function performed by vegetables, and subservient to the formation of their several products. Were the sap which they absorb, and which is conveyed

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* Recherches, p. 194.

† T. Saussure Recherches, p. 101. 109.

‡ Ibid. p. 116.

|| Ibid. p. 126.

through their vessels, merely changed by the function of respiration and the action of light, one product only could be formed from it in each plant; but very different products are formed and deposited in different parts of the vegetable; and the formation of these must be regarded as depending on the action of the vessels, and therefore as arising from a function analogous to secretion in animals. The organs in which this is performed are not well determined. The utricles, or those bundles of vessels found in the stem and other parts, have been considered as secreting glands; but this is not established by any proof. The secreted substances are probably designed to serve some purpose in the economy of the vegetable, or to protect it from external noxious agents. They constitute the principal proximate principles of plants.

After these observations on the functions of vegetables, we have to trace, as far as can be done, the operation of those substances which are received into the vegetable system, and those processes by which these are converted into the varieties of vegetable matter.

The seeds of vegetables consist of two essential parts,—of the Germ, or small bud, the part endowed with life, and the rudiment of the future plant; and of the Cotyledons, or seed lobes, which are connected with it, and which, in the developement of its powers, and the first stage of its growth, appear designed to afford to it nutritious matter. In the germ two distinct parts are discoverable,—the radicle, which descends from the seed, forming the root, and the plumula forming the stem; and it is connected with the cotyledons by slender vessels, which ramify through their substance, and which unite at their *connection with the germ. When the seed is planted in the ground, or placed in other situations favourable to its vegetation, it absorbs moisture, and swells;* the radicle begins to shoot out, and, at the same time, the substance of the seed lobes suffers a change in its qualities, the fecula of which it principally consists being converted into sugar. This constitutes the vegetable function of germination, the first stage of vegetation, and, when performed on certain grains preliminary to fermentation, the process of malting. From its connection with these processes, it has been repeatedly examined, and the principal facts with regard to it have been determined.

It has been ascertained, that the presence of oxygen is indispensable to germination. If seeds moistened are placed *in vacuo*, they do not germinate; as was long ago ascertained by Boyle, in his experiments with the air-pump. If they are confined in nitrogen gas, hydrogen gas, carbonic acid, or nitric oxide gas, or if they are placed over quicksilver, germination does not take place. When immersed in water from which the atmospheric air is excluded, they swell, and the radicle is formed, but vegetation makes no further progress. And in all these cases, if the seed has been moistened, the life of the germ is soon lost, the matter of the seed decomposes and becomes putrid, and a portion of gas, consisting of carbonic acid, with a little carbonic oxide or carburetted hydrogen, is disengaged. These facts have been unequivocally determined, by the repeated experiments of Scheele *, Achard,

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* Treatise on Air and Fire, p. 151, 152.

Ingenhousz *, Gough †, Cruickshank ‡, Huber ||, and Ellis ¶.

When atmospheric air or oxygen is admitted to the moistened seed, germination soon commences, and, at the same time, the oxygen is consumed, and carbonic acid is formed, as appears to have been first ascertained by Scheele, and as has since been established by the experiments of all those who have investigated this subject. The germination is even more rapid in oxygen than in atmospheric air, as Huber ascertained, both by exposing seeds moistened to oxygen gas §, and by placing them, in a comparative experiment, in common water, and in water impregnated with oxygen *. It was likewise found by Humboldt, that seeds which from having been long kept did not germinate when moistened and exposed to atmospheric air, began to germinate when moistened with water impregnated with oxy-muriatic acid, which afforded oxygen to them in a more condensed state, and that, by the application of the same liquid, the germination of seeds in their usual state was always accelerated †,- facts which have been confirmed by Von Uslar ‡ and T. Sau

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* Journal de Physique, tom. xxviii. p. 63.

† Manchester Memoirs, vol. iv. p. 310.

‡ Rollo on Diabetes.

|| Mémoires sur la Germination.

¶ Inquiry into the Changes effected in Atmospheric Air, by Germination, Vegetation, and Respiration.

§ Memoires sur la Germination, p. 19.

* Ibid. p. 141.

† Philosophical Magazine, vol. i. p. 309.

‡ Observations on Plants, p. 138.

sure *. Huber found, however, that although oxygen gas accelerates germination, it proves rather prejudicial to the *progress of vegetation, when the parts of the embryo plant begin to expand; and in twenty-four hours, it was necessary to remove the oxygen gas, as otherwise the radicles became brown and decayed* †. The presence of a little carbonic acid gas with the oxygen gas, he found rather useful, probably by diluting it; for in atmospheric air, the progress of germination is rather favoured if the carbonic acid be withdrawn as it is formed, as Saussure found; and a large proportion of it was found by Huber to be hurtful, even when oxygen was present ‡.

Scheele observed, that during germination, the volume of the air is not sensibly altered, or the oxygen gas consumed is replaced by an equal volume of carbonic acid gas,—a fact which was afterwards ascertained with precision by Cruickshank. It has also been established by Saussure, who has farther endeavoured to show, that the quantity of oxygen which disappears in germination is that which is necessary to the production of the quantity of carbonic acid that is formed. In his calculation, however, on which this conclusion is founded, the quantity of oxygen contained in atmospheric air is stated too high, as Mr Ellis has remarked,—an error arising from his taking Lavoisier's estimate of the proportion, as being $\frac{27}{100}$, instead of $\frac{21}{100}$, as Saussure himself found it to be, by the phosphorus eudiometer ‖. Mr Ellis, in making the experiment, obtained a result very nearly corresponding with that obtained by Cruickshank; the volume of carbonic acid gas produced being nearly equal to that of oxygen gas consumed: a small diminution was perceived, not exceeding one-tenth of the volume of oxygen consumed, and not greater, therefore, than what might fairly be ascribed to the slight condensation oxygen experiences in its combination with carbon *.

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* Recherches, &c. p. 4.

† Mémoires sur la Germination, p. 20.

‡ Mémoires sur la Germination, p. 55. 75. 78.

‖ Philosophical Magazine, vol. vii. p. 158.

The fact, then, established by these experiments, that the quantity of carbonic acid gas produced in germination corresponds with the quantity of oxygen gas which is consumed, leads to the conclusion, that in this process no part of the oxygen which disappears is absorbed by the matter of the seed, or enters into combination with any of its principles, but that it merely abstracts carbonaceous matter, so as to be converted into carbonic acid.

Some chemists, however, have been disposed to conclude, not only that carbon is abstracted from the seed in germination, but that a portion of oxygen enters into combination with its remaining elements, so as to form the saccharine matter which is the product of that process. Thus, Mr Cruickshank, from considering that carbonic acid is evolved from moistened seeds when oxygen is not present, as when they are placed in nitrogen gas,—a fact ascertained by his own experiments, and since by those of Huber †,—supposed, that the formation of this

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* Inquiry, &c. p. 9. &c.

† Mémoires, &c. p. 170. 175. He farther ascertained, that when seeds are placed in hydrogen gas, a portion of carburetted hydrogen is formed.

acid is owing to the decomposition of the water, the oxygen of which combines with carbon from the seed; that therefore, in germination, the same changes will happen; and that the quantity of oxygen which disappears is in part absorbed, and enters, with perhaps a proportion of hydrogen from the water, into the composition of the saccharine matter formed in this process. This reasoning, however, is not very conclusive; for, admitting that water is decomposed by humid seeds, when oxygen is excluded, it does not follow, that this will happen when oxygen is present, and exerting its chemical affinities.

That in germination the matter of the seed not only suffers an abstraction of carbon, but receives an accession of oxygen, may, however, be inferred with some probability from the chemical composition of sugar, the substance which is formed during this process. It contains a large proportion of oxygen, not less, according to Lavoisier's estimate, than 64 in 100 parts; and this large proportion can scarcely be supposed to arise merely from the increase in the relative quantity of this principle, from the abstraction of part of the carbon of the fecula of the seed.

The question, whether, besides the abstraction of carbon which takes place in germination, there is an addition of oxygen to the matter of the seed, might be determined, by ascertaining whether seeds which have germinated lose weight, and whether this loss is exactly equal to the quantity of carbon which has been abstracted, estimating this from the quantity of carbonic acid produced. The determination of this, however, is difficult; for, during germination, seeds always exhale part of the water with which they have been moistened; and it is difficult to estimate the loss of weight they sustain from this cause, and which must modify what they may lose or gain from the other chemical changes connected with the process. Saussure states, that a seed, brought after germination to the same state of dryness as before that process, not only always weighed less, but the diminution of weight was even greater than could be accounted for by the carbon abstracted during the germination, and the small quantity of mucilage that might be dissolved by the water in which the seeds had been macerated. Thus, he placed a number of peas, weighing 200 grains, over mercury, with five times their weight of distilled water, in a jar filled with atmospheric air. They germinated; and, at the end of two days, 4½ cubic inches of carbonic acid were formed, containing, according to Lavoisier's estimate of the composition of carbonic acid, 0.85 grains of carbon; the water in which they had germinated had dissolved a little extractive or mucilaginous matter, which by evaporation was found to amount to 0.75 grains. The seeds, in drying, still continued to form carbonic acid, in quantity rather less, as appeared to Saussure, than what was formed at the same temperature, and during the same time, in germination. Assuming it, however, to be the same, the seeds having required two days to dry, it followed, that in that time they must have formed other 4½ cubic inches of carbonic acid, or lost 0.85 grains of carbon. The total loss, therefore, by abstraction of carbon and mucilage from the seed, amounted to 2.45 grains; and when brought, after the germination, to their original state of dryness, they ought just to have been this much loss in weight, or have weighed 197.5 grains, had the change they suffered consisted merely in the abstraction of carbon; while, had they received oxygen from the water the loss must have been less, or there might have even been, on the whole, an increase of weight. Saussure found, however, that they weighed only 189 grains, or 11 grains less than they did in their original state *. Now, this result renders the whole experiment doubtful; for since the loss of weight amounts to 8.5 grains more than what can be accounted for by the quantity of matter ascertained to have been abstracted, it proves, either that the experiment had been inaccurate, or that a quantity of water had been dissipated, and that the seeds had not retained the same quantity after germination which they had contained before. Saussure supposes, that, during the drying, part of the oxygen and hydrogen of the seed had combined to form water, which had exhaled. Whether this be admitted or not, the result is such, that no certain conclusion can be drawn from it.

The experiment, to determine, whether seeds lose weight by germination, had been before made by Mr Gough, in a manner less liable to fallacy. He placed 7 drachms 23 grains of steeped peas in a phial, the mouth of which was covered with a piece of clean glass, intended to condense the vapour that might arise from them, while the free access of air was not prevented: at the end of one hundred and twenty hours, the peas were found to be vegetating freely; and on weighing the whole, and making the necessary deductions for the bot-

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* Recherches, p. 16.

tle and glass, they were exactly their original weight *. It can scarcely be imagined, that, in this mode of making the experiment, the carbonic acid into which the oxygen of the air would be converted by germination, would remain in the phial: it must have been gradually removed, and its place supplied by atmospheric air; and hence the experiment appears to establish, as Mr Gough stated, that the germination of seeds is attended with little, if any, diminution of weight. It might even warrant the conclusion, that there is an actual increase of weight; for, in this imperfect method of closing the phial, a portion of the watery vapour exhaled by the germinating seed must have escaped.

Mr Gough observed, that when, in the course of the experiment, he withdrew the air frequently from the phial, by inspiring it through a syphon, there was a considerable diminution of weight, not less than 2 drachms 5 grains, when 1 ounce 3 drachms of steeped barley were operated on; owing, probably, as he remarks, to the watery vapour arising from the germinating seeds having been withdrawn.

The subject requires farther investigation; but there appears, so far as the fact is yet ascertained, some reason to believe, that, in germination, besides the abstraction of carbon by the action of the oxygen of the air, there is a decomposition of a portion of the water, and an addition, from this decomposition, of oxygen and hydrogen to the matter of the seed.

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* Manchester Memoirs, vol. iv. p. 316.

To favour the chemical changes which constitute this process, certain circumstances are necessary. A due degree of humidity is essential, seeds which are dry not germinating. It probably operates, by favouring the condensation of the oxygen, and its approximation to the matter of the seed. Though the dry seed may be pervious to any elastic fluid, the elasticity of the oxygen in its aërial form will counteract the affinity it would exert to the carbon : but when the seed is moistened, the water expanding the dry substance, and condensing a minute proportion of the oxygen, will approximate it to the matter of the seed, and thus ſavour its combination with the principle to which it exerts the most powerful affinity ; while the carbonic acid formed from this combination will assume the elastic form. We accordingly find, that in every case, the action of oxygen on vegetable matter is favoured by that matter being in a humid state. Some chemists have considered the evolution of the carbon as the first action that takes place in germination, and that its combination with the oxygen gas is posterior to this evolution, and is not, therefore, strictly essential to germination, but is rather a consequence of it. For this opinion I confess I perceive no grounds : the action of the oxygen appears to be the efficient cause of the abstraction of the carbon ; the chemical affinity between them causing their combination, leaving the other elements in that proportion and condition which produce saccharine matter, while the circumstances which ſavour these combinations, particularly heat and moisture, equally favour the evolution of the germ.

A certain temperature is essential to germination. If it be below the freezing point of water, no seeds vegetate; and the greater number require a temperature considerably higher. This is conspicuous in the germination of seeds commencing and proceeding with rapidity, when the genial temperature of the spring succeeds the winter's cold; and likewise in the seeds of many plants not germinating in cold, as they do in warm climates. The heat probably both excites the vital powers of the germ, and favours the chemical changes of the seed.

Light, too, has an important influence in germination, not, however, in forwarding, but rather in retarding it. It has been long known, that in the process of malting, which is nothing more than germination conducted with a particular view, the admission of light is hurtful; and hence it is always conducted in darkened apartments: and it has been repeatedly ascertained, by direct experiment, that germination is impeded by light. Ingenhousz remarked, that the seeds exposed to the solar light either do not germinate, but die, or, if they germinate, the plants are extremely weak.*. It has been imagined, that the light operates merely from the temperature it excites dissipating the moisture; but any effect of this kind, except from the direct action of the solar rays, must be trivial. As light, by its chemical agency, is always an antagonist to the combination of oxygen, and as this combination, at least with the carbon of the seed, is necessary to germination, it is probably to this operation that the influence *it has on the process is to be ascribed*.

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* { Journal de Phyſique, tom. xxviii. p. 90.
{ Experiences sur les Vegetaux, tom. ii. p. 23.

By the chemical changes which occur in germination, the fecula of the seed is converted into saccharine matter. Its taste becomes quite sweet; and it affords a portion of sugar, on maceration in water. This saccharine matter appears to serve as nourishment to the infant plant; for, being soluble in water, which the fecula is not, it is capable, in this state of solution, of being absorbed by the vessels of the radicle, which begin now to expand, and which ramify through the substance of the seed; and thus, in the first stage of its growth, the plant has a supply of nutritious matter, independent of any external source. Mr Gough, who stated this view of the operation of germination in contributing to the growth of the plant, observes, that it is confirmed by some experiments made by Malphigi, in which, when the germs of seeds were abstracted from the seed lobes, and planted in the earth, very few of them grew, and those that did, grew very imperfectly. This experiment was also performed by Bonnet. The seed having been previously softened, by being kept humid for a few days, he cut the two bundles of fibres which connect the germ with the seed-lobes: he planted the germ in a quantity of garden earth, which was frequently supplied with water: they emitted the radicle, and even at length their leaves; but the plants were so diminutive, that they could scarcely have been recognised, and they soon died *.

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* Bonnet sur l'Usage des Feuilles, p. 239.

From the nature of the changes which thus proceed in germination, and which are absolutely indispensable, as preliminary to vegetation, we can assign the theory of those operations on the soil which constitute some of the principal practices of agriculture. When the ground is ploughed, its cohesion is broken; it is divided into loose particles; and hence, when the seed is sown, it is placed in the most favourable situation for vegetation: it is supplied with moisture, without being immersed in water: its temperature is in some measure kept uniform: the operation of light is at least partially excluded; and, from the looseness of the earth that covers it, the atmospheric air finds ready access to it, and thus promotes the germination and commencing vegetation. When the fibres of the root expand, they meet with little resistance, and are equally supplied with water and air.

When germination has been accomplished, and a source of nutritious matter supplied, capable of being absorbed by the embryo plant, its structure begins to be developed, and its living functions to commence. The radicle first extends, penetrates the soil, and increases in length; not, however, by the mere extension of its fibres and vessels, but by new parts added to its apex, the nutritious fluid from the cotyledons being conveyed to the radicle, and forming these parts. In a short time, the part of the germ named the plumula likewise extends, and rises from the ground to form the stem; and these directions of these parts take place in whatever position the seed has been placed. The different parts are now successively unfolded, according to the nature and structure of the plant.

Its nourishment, after this first stage of its growth, is to be derived from without. This nutritious matter is received principally from the soil and from the surrounding air; and the first object of inquiry in the investigation of the theory of vegetation, is the relation subsisting between these and the growing plant.

By far the greater number of vegetables arise from the earth, and receive from it a large share of their nourishment. It was at one time very generally imagined, that the soil itself afforded them the principal nourishment: it contained, according to the received opinion, certain salts, oils, and earths: these, it was supposed, were absorbed, and formed the principal part of the vegetable matter.

There were always, however, some objections to this theory, and some facts known, particularly those relating to the influence of water in promoting vegetation, which led to a different view. And when chemistry had advanced so far as to accomplish the vegetable analysis with some degree of accuracy, it was discovered, that the solid substance of plants, as well as their various products, are composed in general of principles very different from those contained in the soil.

It was sufficiently known, that many vegetables flourish and increase in bulk when supplied with water alone; and it had likewise been often ascertained, that if a plant be made to grow in a known quantity of earth, the earth after a certain period, during which the plant may have increased greatly in bulk, is found to have lost little of its weight. The celebrated experiment by Van Helmont, appears sufficiently to establish this fact. He planted a willow weighing 5 libs. in an earthen vessel filled with dried earth, which had been carefully weighed. The pot was sunk in the earth, covered with a plate of lead, and rain-water was occasionally conveyed to it through a tube of lead, which passed through the cover. At the end of five years, on removing the tree, it weighed 169 libs., while the earth in which it had been planted, on being dried and weighed, was found to have lost only 2 ounces of its original weight. A similar experiment was made by Mr Boyle. The seed of a gourd was put into earth in a pot, and supplied with water; the plant which grew from it, in the course of a few months, weighed 2¼ libs., yet the earth had not lost sensibly in weight *. These experiments have been repeated and diversified by modern chemists. Duhamel caused plants to grow, by supplying them merely with water, and they flourished sufficiently well †. Tillet found, that wheat and other grains grew in river sand, in pounded quartz, or in mixtures of silex, argil, and lime: they produced seeds, which sown again produced new plants, and this for three successive years ‡. Bonnet found, that plants supported on moss, cotton, or paper, grew when supplied with pure water, and produced flowers and fruit equal to what they produced when growing in the soil. Mr Hoffman inclosed sprigs of the Mentha crispa in phials filled with distilled water, securing the mouths of the phials by a cement of wax. The sprigs in this situation continued to grow, new roots

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* Boyle's Works, vol. i. p. 494, 495.

† Memoires de l'Acad. des Sciences, 1748.

‡ Ibid. 1772, p. 229.

and branches were formed, until the whole of the water had passed through the plants; and on weighing them they were found to have gained considerably in weight *. Boyle had before made this experiment, and had found, that in less than a month a sprig of mint growing in distilled rain-water, increased to nearly four times its original weight †.

It has also been justly observed, that parasitic plants, and those which are attached to stones and rocks, can derive none of their nourishment but from water and air.

These facts appear to authorise the conclusion, that air and water furnish the principal part of the food of vegetables, and that many can live and grow on these alone.

Previous to the discovery of the composition of water, it was difficult to conceive how it could be converted into the solid matter of plants. Much of that matter indeed, as well as of the various vegetable products, consists of water; but it contains also other elements with which this water is combined, and which must even bear a certain proportion to it. The discovery of the composition of water and of carbonic acid, in a great measure solved these difficulties, and shewed how water and air might supply the elements of vegetable matter.

These elements are principally oxygen, hydrogen, and carbon. Water, if decomposed by the powers of the plant, will furnish the two former; and as the atmosphere always contains a portion of carbonic acid, this, absorbed

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* Von Uslar on Plants, p. 100.

† Boyle's Works, vol. i. p. 621.

by the leaves, or even by the medium of water by the roots, may afford the carbon with which these are combined.

That water is decomposed in the process of vegetation, appears to follow from their being no other source whence the hydrogen of plants supplied only with air and water can be derived. It appears also to follow from the fact already stated, as established by the experiments of Ingenhousz and others, that when the leaves of vegetables are exposed to light, in contact with pure water only, they afford oxygen gas,—a proof that their vessels are able, when assisted by the action of light, to decompose a portion of the water which they absorb. It has appeared indeed, from the researches of Sennebier and Woodhouse, that the production of oxygen in this experiment, is considerably dependent on the quantity of carbonic acid contained in the water, or that at least by increasing the quantity of this acid a larger quantity of oxygen is evolved. It cannot, however, depend solely on this; on the contrary, the water itself undoubtedly suffers decomposition, and is the source, in part at least, of the oxygen. This is evident from the fact, that the portion of carbonic acid in common water is so inconsiderable as not to be appreciable; yet leaves exposed, immersed in such water, to solar light, afford oxygen. Ingenhousz found also, that though in boiled or distilled water the quantity emitted was less than in spring water, yet still a certain portion was evolved; and the apparent difference in the proportion was in part owing to the boiled water absorbing a portion of the air emitted*. This air was also purer oxygen than the air from spring water, and this has been also very clearly established by an experiment made by Mr Davy. He filled a glass cylinder of the capacity of ten cubic inches, with mercury. Two small vine leaves were introduced through the mercury, so as to detach all atmospheric air from them. The mercurial apparatus was inserted in a vessel of cold water. Aqueous vapour, was passed from a vessel containing water which had been long in ebullition, through a tube into the cylinder, where it was condensed by the cold mercury, and thus the cylinder was filled with water which held no air in solution. It was then exposed to light. In a very short time air globules began to form on the leaves, and in about six hours two cubic inches and a half were collected, which proved to be nearly pure oxygen *.

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* Philosophical Transactions, vol. lxxii. p. 426.

In this experiment, it is evident, that the oxygen could have been derived only from the decomposition of the water; and the argument already stated, that, from no other source than from the decomposition of water, can the origin of the hydrogen contained in plants which grow when supplied with water and air alone, be derived,—is a sufficient proof, especially when corroborated by such experiments, that this decomposition is effected in the process of vegetation. The quantity of oxygen emitted, too, is greater than could be produced if the water were not in part decomposed. At the same time, it may be admitted, what is very justly observed by Saussure, that this decomposition will not take place to a great extent, unless the plant is at the same time supplied with car-

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* Beddoes's Medical Contributions, p. 159.

bonic acid. The quantities of oxygen and hydrogen can probably not increase in plants beyond certain limits, without the proportion of carbon increasing in the same ratio; and hence in pure water the decomposition, so as to give rise to the fixation of these elements, must take place to a limited extent, and must soon cease. But when carbonic acid is applied at the same time in the necessary proportion, the decomposition of the water will proceed; and accordingly he found, that when plants were supplied with water alone, without carbonic acid being present in the air in which they were kept, they acquired weight, but lost nearly the whole of it again by exsiccation,—a proof that in this case a portion of water had been merely imbibed and incorporated with their substance, without its elements being fixed to any considerable extent, in the composition of the vegetable matter; but when both water and carbonic acid were supplied, they increased their dry vegetable matter in a quantity greater than what could arise from the elements of the acid alone. He concludes, that when vegetables thus fix the elements of water in their composition, they retain both the hydrogen and oxygen; and that the oxygen exhaled by their leaves under exposure to light, arises from the decomposition of carbonic acid *.

That plants decompose carbonic acid, is established by a proof similar to that which establishes the decomposition of water in vegetation,—that there is no other source whence the carbon of plants growing in water and air can be derived. It is also established by more direct proof.

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* Recherches, p. 225, &c.

It has appeared from the experiments of Sennebier, Saussure and others, that in an atmosphere composed partly of carbonic acid, the leaves of plants absorb and decompose a portion of it: and as carbonic acid is always present in the atmosphere, it is probable that from this source vegetables derive at least part of their carbon. Saussure accordingly found, that plants growing in pure water, and in atmospheric air not deprived of the small portion of carbonic acid which it naturally contains, increase their quantity of carbon, as has been already stated (page 46.) A portion of carbonic acid is also probably absorbed by their roots in solution in water. Sennebier found likewise, as has been stated, that when growing vegetables were supplied with water impregnated with carbonic acid, they afforded more oxygen under exposure to light, than when supplied to an equal extent with pure water,—facts confirmed by the experiments of Ingenhousz and Woodhouse, already referred to, (page 36.): and according to Saussure, although water impregnated with carbonic acid is rather unfavourable to vegetation in its earlier stages, it afterwards favours it, so that plants supplied with water thus impregnated, weigh more after a given period, than those supplied with pure water*. It is probable, that plants are naturally furnished with a large proportion of carbonic acid in this manner. It is in a constant state of production at the surface of the earth: being absorbed by water, it must be conveyed in a certain quantity to the roots of plants, by which it will be absorbed.

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* Recherches, p. 27.

The influence of the other constituent principles of the atmospheric air in promoting natural vegetation, is less clearly established. That of the nitrogen of the atmosphere appears to be entirely negative; and as oxygen appears to be emitted by plants when their vegetation is probably most vigorous, that is, under the action of light, it might be concluded that it will not be absorbed. Experiments have been stated, however, which prove, that plants grow much more vigorously when supplied with water impregnated with oxygen, than when common water was used *; and the fertilizing influence of dew has been ascribed to the saturation of the water with the oxygen of the air through which it has slowly descended. T. Saussure found, that when the roots of plants were exposed to carbonic acid gas, to nitrogen, or hydrogen gas, they died in thirteen or fourteen days, while, when exposed to atmospheric air, they continued to flourish. He found also, that they consume the oxygen of the air in a quantity equal to their own volume, and form carbonic acid. When the roots of the vegetable were not detached, but remained in connection with the stem and branches which were placed without the jar in which the roots were confined with atmospheric air, they absorbed many times their volume of oxygen gas, which appeared to be conveyed through the plant, and delivered by the leaves to the external air. Saussure concludes, that the contact of oxygen with the roots, is useful to vegetation. Hence many plants require a loose soil, and are more vi-

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* Experiments by Sir Francis Ford, Philosophical Magazine, vol. i. p. 109. 224.

gorous when their roots are not covered with too much earth *. The principal advantage derived from oxygen thus applied, is perhaps from the stimulus it communicates to the vessels of the plant.

From the preceding facts it appears, that air and water may furnish, and probably do furnish the largest portion of the food of plants.

In their decomposition, however, in the vessels of vegetables, another agent is concerned, and appears indispensable. This is Light. When it is excluded, plants become pale and feeble, and their usual products are no longer formed. It is not by the heat which light excites that it is favourable to vegetation, for the same effects are not obtained when heat is applied without the admission of light. It may operate partly by acting as a stimulant in relation to the irritability of the vegetable, and thus exciting its vessels to increased action; but this cannot be its sole operation, as the substitution of other powerful stimulants ought, for a time at least, and to a certain extent, to be productive of the same phenomena, which is not the case. It must therefore in part operate as a chemical power. Of the precise nature of its operation we must remain uncertain, while the question is undecided, whether light is a component part of inflammable bodies or of oxygen. If the latter supposition be made, it may be concluded, that while the vegetable matter existing in the sap exerts attractions to the carbon of the carbonic acid, and the hydrogen of the water, the light exerts affinities to the oxygen of both, and by these united

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* Recherches, p. 104. 109. 111.

forces their decomposition is effected. Or if light be supposed to be a component part, not of oxygen gas, but of inflammable substances, it must be concluded, that while the vegetable matter attracts on the one hand the carbon and hydrogen of the carbonic acid and water, but with a force insufficient to decompose them, the light at the same time exerts attractions to these elements, and these concurrent affinities may be sufficiently powerful to effect the decomposition. The action of light is exerted principally on the sap circulating in the leaves of plants; and when vegetables which have been blanched by seclusion from light are again exposed to it, the green colour appears first towards the margin of the leaf. It is in the leaf, therefore, that the principal chemical changes from which the formation of vegetable matter arises take place. It is well adapted, by its position, to admit of the agency of light; and its structure is probably sufficiently porous to admit of the passage of those aërial fluids, which it either absorbs from the atmosphere, or evolves as the result of the decompositions which happen in the fluid circulating through its minute vessels.

We are thus presented with the most simple view of the theory of vegetation. The vegetable by its own powers, assisted by the agency of light, decomposes a part of the water and carbonic acid which it receives. The carbon and hydrogen of these, with part of the oxygen, are expended in the formation of the vegetable products, while the superfluous oxygen is discharged by the leaves. A small portion of the nitrogen is likewise perhaps absorbed; and either from combinations of these elements, or from the water absorbed by the roots, may be derived the trivial quantities of saline and earthy substances which are found in vegetable matter.

This view rests altogether on the admission, that in vegetation water and carbonic acid are decomposed; but even with this admission it has been doubted if it is just. Some chemists have called in question the conclusion, that vegetables grow when supplied with air and water alone: they have endeavoured to prove, that though there may be an enlargement of size or developement of parts, this is not perfect, and there is no increase of vegetable matter; and they have also endeavoured to shew, that the experiments from which that conclusion has been drawn, are liable to sources of fallacy sufficient to invalidate the conclusion itself.

Hassenfratz, some years ago, stated these objections to the experiments of Van Helmont, Duhamel, and Tillet, and, in confirmation of his objections, gave the results of experiments on various plants which expand when merely supplied with water, as hyacinths, kidney-beans, cresses, and others. They grew in this situation, or their parts were unfolded; but even this growth was imperfect; the vegetation advanced no farther than the production of the flowers, without the seeds being formed, or at least without their coming to maturity; and these plants when dried and analysed, afforded, as he states, rather less carbon than was contained in the seed or bulb from which they had been reared *.

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* Annales de Chimie, tom. xiii. p. 185, 188.

Experiments with a similar result have been made by T. Saussure. He endeavoured to bring into a state of vegetation the seeds of the kidney-bean, the common pea, cresses, and similar plants, by supporting them on fine sand, and supplying them with distilled water. They frequently flowered, but their seeds never came to maturity[*].

Mr Knight has also observed, that bulbous and tuberous rooted plants contain within them the matter which serves for the developement of their parts; and that when they grow on being supplied with water, the water, if perfectly pure, operates, not by supplying them with new matter, but only by dissolving and distributing through the expanded plant, the matter which had been contained in the root[†].

To the experiment of Van Helmont, and others of a similar kind, the objection has been made, that in the period requisite to the growth of the plant, the water with which it had been supplied must have conveyed to it a quantity of foreign matter. Thus Bergman remarked, that even rain-water, with which the willow in Van Helmont's experiment was supplied, contains a small portion of earthy matter, which by the constant supply would accumulate in the plant, in quantity sufficient to afford all the earth it contained at the termination of the experiment[‡]. And Kirwan afterwards remarked another source of fallacy, that the pot containing this willow being earthen and of course porous, and being placed in the soil, a quantity of water from the soil, and conveying matter from it, must have percolated the vessel, and been absorbed by the roots of the tree *. A similar source of fallacy, it has been observed by Hassenfratz, existed in the experiments of Tillet †.

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[*] Recherches, p. 245.

[†] Philosophical Transactions, 1805, p. 97.

[‡] Opuscula Physica, vol. v. p. 92.

The observations and experiments now stated may prove, that plants supplied with water alone will not grow. They indeed cannot, as there is no source whence the carbon essential to the formation of their substance can be derived. They may even prove, that to some plants the supply both of air and water is insufficient, and that these are incapable of vegetating properly, without matter derived from the soil. But they are altogether insufficient to render this conclusion general, or to invalidate the opposite conclusion, that vegetation may be supported by air and water alone, and that many plants supplied with these will flourish, and form their peculiar products.

The facts which establish this last conclusion are numerous, and on a scale which scarcely admits of any fallacy. It can scarcely be doubted indeed, when we consider the circumstances connected with the growth of a large vegetable, as of any of our common trees. Their roots extend to no great extent or depth in the soil, and that soil does not require to be renewed, or to receive any supply of manure. Nay, frequently the situation is such, that

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* Essay on Manures, p. 80.

† Annales de Chimie, tom. xiii. p. 187.

scarcely any manure or nutritious matter is afforded, or any thing but a support by which the plant is exposed to the air, and occasionally supplied with water, as in the example of those trees which grow from the crevices of a rock, frequently on the very face of a precipice. Yet, in all these situations, the growth of the tree advances, its solid matter increases, and, in many of them, much vegetable matter is annually lost in the fruit, or the fall of the foliage. It is obvious, that the portion of soil with which the plant can be supposed to communicate, could not have originally contained the matter from which this increase is derived; and there is no external supply but from the atmosphere, and from water. The atmosphere, so far as we can discover, can afford little to vegetables directly nutritious, or capable of furnishing the elements whence their products are formed, except carbonic acid, and water applied under such circumstances, can afford, independent of its own elements, only a small portion of saline and earthy substances, which, from what we know of the analysis of vegetable matter, cannot be very essential to its formation. We are reduced, therefore, in this case, to the conclusion, that the carbon, hydrogen, and oxygen, which form not only the basis, but almost the entire substance of the vegetable, must be derived from water and atmospheric air.

The objections that have been made to Van Helmont's experiment, and others of a similar nature, are of no force against this conclusion. They invalidate only the absurd position, if it were maintained, that water alone can be converted into all the products of vegetation. It may be granted, as Bergman has remarked, that a portion of saline matter might be conveyed by the water to the plant; and this may be the origin of the saline matter which it would contain: or, as Mr Kirwan has observed, the water might filtrate from the soil through the vessel, and thus convey some earthy substances, and even some nutritious matter, to the plant. But this must have been in limited quantity in the soil itself; and the communication could not have been so extensive, as to have afforded from this source all the principles which formed the substance of the plant, and which increased it from five to one hundred and sixty-nine pounds in weight.

Lastly, the experiments of Saussure already referred to (page 16.) are conclusive, in opposition to those of Hassenfratz, in proving, that plants acquire an augmentation of vegetable matter, when supplied with air and water alone. If the atmospheric air, indeed, were excluded, or rather, if the small portion of carbonic acid which it naturally contains were removed, by washing with lime-water, the vegetables, as already stated, merely expanded, without any real addition of vegetable matter; but, when supplied with water, and with atmospheric air in its natural state, and fully exposed to light, the proportion of vegetable matter increased with their enlargement of bulk. The opposite results obtained by Hassenfratz were probably owing to the plants not having been sufficiently exposed to light; for, in this case, Saussure found, that the proportion of carbon is even rather diminished than increased.

The two series of facts on this subject which appear opposed to each other,—the one proving, that many vegetables will grow when supplied with air and water alone,

—the other equally proving, that, in such a situation, the growth is imperfect, and is little more than an expansion of their solid matter, may perhaps be reconciled, by considering vegetation under the following point of view.

In plants which expand rapidly, as in those which were the subjects of the experiments of Hassenfratz, or of the observations of Knight, the contact of a rich soil may be necessary to bring them to perfection. The developement of their parts may so far exceed the slow supply of nutritious matter from the decomposition of water and carbonic acid, that they will decay before their vegetation has been completed. But this only proves, that, from the peculiar nature of these plants, the expansion of their parts has been more rapid than the supply of nutritious matter, under such circumstances, can support, while, in others, the growth of which is more slow and gradual, it does not follow but that a sufficient supply of nourishment may be derived from water and atmospheric air.

In vegetables of this last description, under which are probably to be classed all the larger plants, a due proportion in the supply of water and of carbonic acid will no doubt be required. Water alone can furnish only oxygen and hydrogen, and, if it exceed much the proportion of carbonic acid, it probably will not be decomposed; for, without a due proportion of carbon, as Saussure has remarked, oxygen and hydrogen cannot be accumulated in the plant; and, for the same reason, an excess of carbonic acid may not be of any utility, as carbon must equally be incapable of being assimilated without the necessary proportions of the other two elements. In those plants which grow slowly, the growth will probably adapt itself, in establishing these proportions, to the quantities of each which are afforded to it; and, from the general facts connected with their growth, there can be little doubt, that the decomposition of these substances afford the elements whence their products are formed.

It is equally true, however, that, in many vegetables, these are insufficient, and a direct supply of more nutritious matter is indispensable to their proper growth. This is proved by the most familiar facts in agriculture. Many vegetables will flourish only in certain soils. Those which require a rich soil vegetate feebly in a poorer, and they always exhaust that in which they grow, so that it requires to be renewed by certain additions.

In conformity to the view of vegetation which I have just given, it follows, that those plants which grow rapidly must be those that will thus require the most nutritious soil; and that of such as grow more slowly, those will most require it which give the largest produce of seeds or fruit, compared with the plant when these begin to be formed. Hence, those plants which are cultivated for the nourishment of animals, are of all others those which require the most nutritious soil; and the proportion of their products is at least within some limits proportioned to it. It is interesting, and intimately connected with the theory of vegetation, to trace the influence of the substances from which these results are obtained.

The matter which is thus required by many vegetables to enable them to grow and form their various products, must be such as contains the elements of these products, and, at the same time, such as they can absorb and assimilate. Hence the great superiority of decaying vegetable and animal matter. This constitutes what is, properly speaking, the richness of a soil. The crust of earth which forms the soil consists principally of silex, argil lime, and magnesia. According as one or other of these predominates, the soil may be loose, or adhesive; may be calculated to retain water, or to allow it a free passage; or may have various other qualities influencing the growth of plants, and, from such qualities, may be adapted to the support of certain vegetables. But in sustaining the plants which are cultivated for the nourishment of animals, something more is required: it must contain decomposing vegetable and animal matter: its fertility ceases when this has been abstracted, and can only be renewed by a fresh quantity being introduced.

This, therefore, forms the first and most important of the manures. Its nature must vary somewhat, according to the intermixture of animal and vegetable matter; but it must always contain, in large quantity, the elements of which vegetable matter is formed, and indeed must consist almost entirely of these. The black mould into which vegetable matter passes by slow decomposition, and which always exists more or less in the soil, consists principally of the carbon which is the basis of that matter, with portions of the other elements. Saussure, in analyzing it by heat, found it to contain more carbon and less oxygen than unchanged vegetable matter. It appeared to contain also a larger proportion of nitrogen. To water it yields a portion of extractive matter, and a small quantity of carbonic acid; and exposed in a humid state to the atmosphere, it absorbs oxygen, and forms carbonic acid *,

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* Recherches. p. 162

as Ingenhousz, Gough, Humboldt, and others, had before observed.

The great utility of vegetable and animal substances as manure, undoubtedly consists in their affording matter already assimilated, and hence more fit to serve for the nutrition of the vegetable. The water which is present dissolves the mucilaginous and extractive principles, and, being absorbed by the roots, must afford more nutritious matter than water that is pure. Saussure found, that water holding in solution various salts, as well as different vegetable substances, gum, sugar, &c. easily enters the roots of plants by absorption; and that this absorption is in some measure elective, some substances being more largely absorbed than others. The salts thus introduced were afterwards discovered in the plant, on burning it *.

Not only is nutritious matter thus conveyed from the soil by the medium of water; there is also every reason to believe, that the gases which are evolved in the slow decomposition of the vegetable and animal matter mingled with it are in part absorbed. Under such circumstances, carbonic acid, carbonic oxide, and oxy-carburetted hydrogen gases, are formed: portions of these will be retained by the water of the soil, and may even be directly absorbed by the vessels of the root. Mr Knight has accordingly remarked, that in his experiments on the sap of vegetables, it always appeared to contain a large portion of air. The gases thus conveyed into the vegetable contain the elements from which its products are formed,

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* Recherches, p. 252. 260.

and in a state, probably, in which they will be easily combined and assimilated.

Yet the quantity of vegetable matter directly conveyed into the plant, would appear, from Saussure's experiments, not to be considerable. He found, that rain-water, which had stood many days on a soil containing much manure, formed an infusion, which did not contain above one part of vegetable matter to a thousand of water. He found reason to conclude, too, that a plant, in absorbing this solution, would not assimilate above the fourth part of the vegetable matter it contained: hence, it would not increase in weight above a quarter of a pound, from the accession of such matter, in absorbing one thousand pounds of such an infusion, which, in a small plant, would require a very long time *. This conclusion, however, cannot be regarded as very exact; and, independent of the matter directly afforded by manures to the water in the soil, much of the nourishment they afford by the plant is probably by the medium of the gases they evolve.

It may perhaps be affirmed, that vegetable and animal substances furnish the only species of manure directly nutritious, or capable of affording matter which the vegetable can immediately assimilate. But there are others, scarcely less useful, in improving the soil, in promoting the decomposition of the vegetable or animal matter which it contains, or in exciting the plant to more vigorous action.

Of these, the first place is unquestionably due to lime. Its utility is sufficiently known, not only in increasing the

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* Recherches, p. 237.

products of vegetation, but in improving their quality; and various opinions have been offered on its mode of operation. In clay soils, it is obvious that it may prove useful, by rendering the earth more free and loose, more pervious to air and moisture, and to the roots of plants. It may likewise destroy insects, which often prey on the tender vegetable: it may decompose any saline substance which is injurious to vegetation; and it probably acts as a stimulus to the plant arrived at maturity, and thus quickens the process of vegetation. But the principal advantage attending the use of lime as a manure, appears to be derived from its power of hastening the decomposition of vegetable and animal substances, and thus supplying to the plant in greater abundance the different gases capable of contributing to its nourishment. That lime does exert such an operation, is evident, from its reducing even the ligneous matter of plants in a short time to a black mould, when its action is favoured by humidity; and that it is by this operation that it proves useful as a manure, appears to be established by the fact, that its utility is most conspicuous in those soils which abound in animal and vegetable matter; and when this is exhausted, the lime is less useful, until it is renewed.

Some have imagined, that the lime acts in this manner, by directly combining with the vegetable or animal matter, and, in particular, with the carbon of that matter, rendering it soluble in water, and thus conveying it into the vessels of the plant. But there appears to be little foundation for this opinion; nor can it well be supposed, that so much lime as must thus be conveyed, could be received without injury into the vegetable system. In promoting the decomposition of these substances, it seems to act principally by a resulting affinity.

Lime, when united with carbonic acid, has an effect somewhat similar, though in an inferior degree; and, united with sulphuric acid, or under the form of gypsum, it has been used with advantage as a manure, probably from an analogous operation. Even some saline substances have been found to promote vegetation, such as muriate of soda, when added in very small quantity. Duhamel found, that marine plants growing in an inland situation languish, if not supplied with this salt.

The nature of the soil, too, with regard to its earthy and even its metallic ingredients, has an important influence on vegetation, and adapts it to different plants, chiefly by being more or less pervious to the roots, by affording to the vegetable a more or less firm support, and by admitting of the application of air and water in due proportion. The earthy matter of the soil is derived from the disintegration of the rocks over which it lies, or from materials originating from such disintegration, and spread over the surface by the operation of water. It must consist, therefore, of the principles of which the earthy aggregates are formed, and, in different situations, will consist of these in different proportions. Of the earths, silex and argil constitute the basis of every soil; and the qualities of this soil will vary, according as either predominates. A soil in which argil is the chief constituent, or which consists principally of clay, is stiff, and not easily worked: it imbibes water, so as to be thoroughly moistened, very slowly; but, when it has been brought into this state, it retains it strongly, and in drying it contracts and hardens, so as not to admit easily of the extension of the roots of plants, or be very permeable to water and air. Silex seldom exists in large quantity in a soil in a state of very fine division, but in fragments, forming a sandy or gravelly soil. In this, qualities the reverse of those of a clay soil prevail; and hence the adaptation of each to particular plants, as well as the advantage derived from a due proportion of the one to the other. The presence of calcareous earth serves, to a certain extent, the same purposes: it lessens the adhesive quality of the clayey soil, and the porosity and looseness of that in which the silex predominates; and probably is still farther useful, in stimulating the vessels of the root, in attracting carbonic acid, and, as has been already explained, in favouring the decomposition of inert vegetable matter. Magnesia is probably always present in very inferior proportion, and its operation does not appear to be very well marked; though it has been concluded, from some facts, that it is rather hurtful to vegetation, particularly from some kinds of limestone, which on analysis were found to contain magnesia, being prejudicial when used as manure. Oxide of iron is the principal metallic matter present in the soil; and it has been supposed to be in some cases advantageous, by attracting oxygen from the atmosphere.

An extensive series of experiments, on the comparative powers of different mixtures of earths in sustaining the vegetation of those plants which are cultivated for nourishment, was undertaken by Tillet *. He employed large earthen pots, which he sunk in the earth very nearly to

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* Mémoires de l'Acad. des Sciences, 1772, p. 229.

the level of the surface, so that the plants growing in them might be as much as possible in a natural situation, and participate in all the vicissitudes of the season; and, with the same view, he abstained from supplying them with any water, even when, from the want of rain, they seemed most to require it. The experiments on each earthy mixture were continued for three successive years; the grains produced the first year being planted for the second, and those produced the second being in like manner planted for the third. From their general results, it appears, that there is a considerable latitude with regard to the earthy mixtures capable of supporting vegetation. Wheat was the grain that was the subject of experiment; and it was found to grow well in various mixtures of sand, clay, plaster, and fragments of stones, as well, indeed, as in earth taken from a cultivated soil. Nay, it even flourished apparently equally well in sand alone, in fragments of stone, in old plaster or mortar. An excess of argil or clay appeared to be prejudicial, principally by communicating the property of hardening after being moistened, so that water was not easily diffused through it, and the roots of the vegetable met with too great resistance. No great advantage was derived from the addition of marl, and less benefit accrued from the mixture of vegetable and animal manure than might have been expected, from the advantage obviously derived from it in the practice of agriculture. Tillet was disposed to conclude, from considering the results of all his experiments, that water was the most essential agent in promoting vegetation, and that the principal advantage of a soil is to preserve a certain degree of humidity, while, at the same time, it allows the roots to extend freely, and absorb it.

The following analysis of a fertile soil, in a climate in which much rain falls, that of Piedmont, is given on the authority of Giobert. One pound consisted of

Carbonaceous Matter 25 grains
Water 70
Silex from 4362 to 4475
Argil — 509 to 793
Lime — 283 to 679, with a portion of air, about 19 grains, of which one-third was carbonic acid, and the remainder carburetted hydrogen. In less fertile soils, the proportion of silex in the pound Troy was from 2716 grains to 4328, of argil from 396 to 1245, and of lime from 339 to 622. And in barren soils, the proportions were, of silex from 2368 to 4963, of argil from 1128 to 1632, and of lime from 225 to 620. In a drier climate, Bergman found a fertile soil to consist of four parts of clay, three of siliceous sand, two of calcareous earth, and one of magnesia. It appears, from the several analyses that have been made, that the less rain falls in a country, the proportion of calcareous earth in the soil must be increased, and that of siliceous earth diminished, to render it fertile. On this subject, some farther details are given in Mr Kirwan's treatise *. Some facts have been also added by Mr Davy, in his late memoir on the analysis of soils †. The soils that are most

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* Essay on Manures, p. 55, &c.

† Nicholson's Journal, vol. xii. p. 81.

productive of corn, he remarks, contain always certain proportions of argillaceous and calcareous earth, in a finely divided state, and a certain quantity of vegetable or animal matter. The quantity of calcareous earth is, however, very various, and in some cases very small. A very fertile corn soil from Ormiston in East Lothian, afforded to Mr Davy, in an hundred parts, only eleven of mild calcareous earth: it contained twenty-five parts of siliceous sand; the finely divided clay amounted to forty-five parts; it lost nine in decomposed animal and vegetable matter, and four in water, and afforded indications of a little phosphate of lime. Its fertility might be in some measure connected with this last substance, as it is found in wheat, oats, and barley, and may be a part of the food of the plant.

An important result, which appears to be established by some of Mr Davy's analyses, is, that a soil may be fertile though it contain little vegetable or animal matter. A soil from the low lands of Somersetshire, celebrated for producing excellent crops of wheat and beans without manure, he found to consist of one-ninth of sand, chiefly siliceous, and eight-ninths of calcareous marl, tinged with iron, and containing only about five parts in the hundred of vegetable matter: no phosphate or sulphate of lime could be detected in it. And hence, as Mr Davy concludes, "its fertility must have depended principally upon its power of attracting principles of vegetable nourishment from water and the atmosphere." This leads to a very important inference with regard to improving soils. "In supplying animal or vegetable manure, a temporary food only is provided for plants, which is in all cases exhausted by means of a certain number of crops; but, when a soil is rendered of the best possible constitution and texture with regard to its earthy parts, its fertility may be considered as permanently established. It becomes capable of attracting a very large portion of vegetable nourishment from the atmosphere, and of producing its crops with comparatively little labour and expence." Some alteration in its constitution may, no doubt, arise from the mere succession of crops; but any deterioration from this cause might be obviated, by their judicious alternation, or by other methods which occasional analyses would suggest. And these observations undoubtedly lead to a field of research hitherto much neglected, though so highly important.

Mr Davy has justly observed, that the results of analyses considered as affording indications of fertility, must necessarily differ in different climates, and under different circumstances. "The power of soils to absorb moisture ought to be greater in warm and dry countries than in cold and moist ones, and the quantity of fine argillaceous earth they contain larger. Soils, likewise, that are situated on declivities, ought to be more absorbent than those in the same climate in plains, or in valleys. The productiveness of soils must likewise be influenced by the nature of the sub-soil, or the earthy and stony strata on which they rest. Thus, a sandy soil may sometimes owe its fertility to the power of the sub-soil to retain water; and an absorbent clayey soil may occasionally be prevented from being barren, in a moist climate, by the influence of a sub-stratum of sand or gravel."

Besides a proper soil, the due application of heat and light are necessary, as has been already stated, to the process of vegetation,—heat, as a stimulus to excite and sustain the actions of the plants,—light, partly from the same operation, and partly from its chemical powers.

Such are the circumstances most materially influencing vegetation; and the statement of them presents the following general view of the series of chemical changes which constitute this process.

Regarding germination as its first stage, the seed exposed to humidity and atmospheric air expands: its farinaceous matter, by the action of the oxygen of the air, is converted into sugar, which serves as food to the infant plant. Its organs are gradually unfolded, and its nourishment received from a different source: water, pure, or holding vegetable and animal matter in solution, is absorbed by the roots; and, in a soil containing decomposing vegetable and animal matter, different aërial fluids are likewise received, and mingled with the sap. This, in its progress through the root, dissolves even part of the vegetable matter; and from this, the plant, in the first stages of its growth, is better enabled to form its various parts. It is brought to the leaves of the vegetable, and is there presented, under a very extensive surface, covered with a very thin membrane, to the action of the air and light: part of its water transpires; carbonic acid, in minute quantity, is perhaps absorbed; and, by the action of the vessels, assisted by the chemical agency of light, new combinations are established, and the proper juice of the plant is formed. This is conveyed by the footstalk of the leaf, and by vessels proceeding downwards through the bark, or between it and the wood: it is deposited in different parts, or is still farther changed in its progress,—

changes from which the peculiar vegetable products are formed.

For the perfection of this process, the soil must be adapted to the nature of the vegetable; it must permit its roots to extend, allow free access to the air, and convey and retain the necessary degree of humidity; its nutritive powers must in general be increased, by the intermixture of vegetable and animal matter; the decomposition of this must often be accelerated, by the application of other species of manure; and, lastly, all the actions of the vegetable must be excited and sustained by the due proportion of heat and light.

From the principles conveyed by this process to the growing plant, may be derived all the elements of which its products are formed. These consist principally of carbon, hydrogen, and oxygen; and with regard to these, their origin is not at all doubtful. Any compound of nitrogen which may exist in vegetables, is probably formed from that gas, received either from the atmosphere, or by absorption from the vegetable or animal matter in the soil; and the minute quantities of sulphur and phosphorus that appear to exist in some vegetables are probably derived from this last source.

There is rather more obscurity with regard to the earthy and metallic substances found in vegetables, or at least contained in the ashes afforded by their combustion; and different opinions have been held with regard to their origin.

The saline substances afforded by the combustion of plants are chiefly the sulphates, muriates, and carbonates of potassa and of soda, the sulphate and carbonate of lime, and the phosphates of lime and magnesia; and with these are associated small portions of silex, and oxides of iron and manganese. Of all these substances, the alkaline salts are those which are most abundant. Some of them are probably not essential to the vegetable, those especially which are in minute quantity, and not always found in the same plant.

It has been considered as doubtful, whether some of these actually pre-exist in the vegetable matter, or are formed during the combustion by which they are obtained. In confirmation of this last opinion, the fact has been stated, that they cannot be extracted, at least in so large a quantity, by any other process, as they are afforded by burning. Those of them which are compounds may no doubt, in part at least, have this origin; but this conclusion cannot be drawn with regard to those the composition of which is not established. And although they cannot be extracted in equal quantity by the maceration of the vegetable matter in water, owing, probably, to the state of combination in which they exist, Saussure has found, in his extensive researches on this subject, that when plants are washed much with water previous to their combustion, they afford a smaller quantity of ashes than when burnt without being subjected to this preliminary operation.

Admitting the existence of these substances in vegetable matter, the question naturally occurs, are they formed by the process of vegetation, or are they always derived by absorption from the soil? Each of these opinions has been maintained. From so many vegetables growing when supplied with air and water alone, some have been disposed to conclude, that these substances are not conveyed into the plant, but formed in it by the chemical processes connected with its growth; while, in opposition to this conclusion, it has been urged, that, in any experiment made to establish it, the water had not been perfectly free from foreign matter, and that, from the substances water usually holds in solution, these products may have been derived. Many of them, too, there is no reason to regard as compounds, and of course as capable of being formed by combination; as, for example, the different earths and metals which have been found in plants. And some facts have been long known, which prove the connection of the saline matter in vegetables with the soil. Thus, marine plants usually contain muriate of soda, which diminishes in quantity, however, and at length disappears when they are transplanted to an inland situation; and certain plants which contain nitre, as pellitory, borrage, and others, do not flourish but in a soil containing nitrous salts.

The extensive researches of Saussure on the analysis of vegetables, the results of their incineration, and the connection of these with the soil, have thrown much more light on this subject.

He established, in the first place, the important fact, that analysis discovers all these substances in vegetable mould *; and farther, that they exist in solution in water which has macerated on that mould †. He also found, that plants absorb small quantities of saline substances,

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* Recherches, p. 280.

† Ibid. p. 292.

when these are presented to their roots in solution in water *, the quantity absorbed being greater with regard to some salts than with regard to others. Since these substances, therefore, are usually contained in the soil, and since they are capable of passing by absorption into the vegetable system, their presence in vegetables is rather to be expected, and it would even be surprising if they were entirely wanting.

Saussure farther found, by comparative trials on plants supplied with pure water, and with water in which certain salts were dissolved, that the saline matter which had been absorbed remained in the plant, and might be detected in the ashes formed by its combustion †. It likewise followed, from other comparative experiments, that when beans were made to vegetate, by being supplied in one arrangement with distilled water, being planted in another in gravel in glass capsules placed in the open fields and supplied with rain-water, and in a third, being planted in the common soil in pots,—in all these cases, the quantity of ashes they afforded on burning was different; from 100 parts of the dried vegetable matter of the first, 3.9 parts of ashes were obtained; from 100 of the second, 7.5 parts; and from 100 of the third, 12 parts ‡.

In the last place, the proportions of the elements of the ashes have almost always a certain relation to the soil. Plants which have vegetated in a soil that has originated from the disintegration of a siliceous rock, furnish, other circumstances being alike, ashes which contain less lime

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* Recherches, p. 251.

† Ibid. p. 259. ‡ Ibid. p. 281.

and more silex than those which have grown in a calcareous soil. If the soil, however, contain much vegetable mould, this may not happen: the ashes will then be alike. This was established by an experiment made by Lampadius. He prepared in a garden, five spots of four feet square surface, and one foot depth; in each he put a mixture of a pure earth, and of eight pounds of animal manure. He sowed rye-seeds in each; and the ashes of the plants produced were found to contain the same principles. Lampadius concluded from this, that the earths found in vegetables, or at least some of them, are formed in vegetation; but, as Saussure has remarked, the manure not having been analyzed, might contain a sufficient quantity of those earthy and saline substances most congenial to the plant, and which it would absorb *.

All these facts appear in favour of the conclusion, that the saline, earthy, and metallic substances found in plants are derived from the soil.

From this conclusion, Saussure explains very well a number of facts connected with the production of ashes by incineration from vegetables, which otherwise have not been accounted for †. Thus, it has been sufficiently ascertained by repeated experiment, that herbaceous plants afford more saline matter than those which are larger, and have more wood. Now he observes, that according to his experiments, saline matter is conveyed into the plant only by absorption of water holding it in solution, and this only in very minute quantity. It follows, therefore, that those plants which absorb and transpire most should contain the largest quantity of saline matter, as the largest

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* Recherches, p. 283. † Ibid. p. 274, &c.

quantity must be conveyed into their substance. But it is proved, by the experiments of Hales and Bonnet, that herbaceous plants transpire more than those of a larger size.

It may be expected, that the saline matter will be principally deposited in those organs in which transpiration is performed. These are chiefly the leaves; and accordingly, experiment has proved, that, in a given weight, the leaves yield more saline matter than any other part of the plant. The bark, Saussure found, contains more than the interior parts, and obviously from a similar cause.

When the parts of a vegetable, the leaves for example, are washed repeatedly with water, they afford a smaller quantity of ashes on burning, than when burnt without this previous washing.

It is to be added to this general statement, that although these principles are chiefly derived from the soil, Saussure found reason to conclude, from some experiments, that the atmosphere may afford a portion of them. The experiment by which this was to be determined was, obviously, to cause grains to grow in distilled water, and, by a comparative experiment, to determine whether the plants produced afforded more saline or earthy matter than was contained in the seed. On making the experiment, it was found, that there was a small increase of this matter during the vegetation, which, according to the views of Saussure, had probably been deposited from the atmosphere on the leaves of the plant *.

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* Recherches, p. 304.

CHAP. II.

OF THE PROXIMATE PRINCIPLES OF VEGETABLES.

IF the chemist, in the examination of the products of the vegetable kingdom, were under the necessity of investigating the properties and composition of the individual substances produced by every plant, the task, from its extent, could scarcely be executed. It is one, however, which is altogether unnecessary; for however numerous and diversified the products of vegetation may appear to be, they are all reducible to a few species, capable of being distinguished by appropriate characters. These form what are named the Immediate or Proximate Principles of Plants: they are obtained directly by a very simple analysis, and are all compounds formed by the combination of the ultimate elements of vegetable matter.

Thus, suppose that the object of the chemist is to discover the composition of the bark of any vegetable, he does not attempt to resolve it at once into its ultimate elements, since from this, without an intermediate analysis, little information would be gained. But he endeavours to discover of what immediate principles, capable of being separated and distinguished from each other, it is composed. If, with this view, it be subjected to maceration in water, it will probably communicate to the water colour, taste, and other sensible qualities. If the remaining bark be next heated with water in close vessels, a portion of fluid distils over, from which, on standing, an oily matter may separate, possessing odour and taste in an eminent degree. If the matter which remains is digested in alkohol, a substance may probably still be extracted, which had hitherto resisted the action of the water; and by repeated experiments of this kind, nothing is at length left, but the inert ligneous fibre. If it be now inquired, what was the composition of the bark, the analysis warrants the conclusion, that it consisted of a peculiar matter soluble in water; of another, not soluble to any extent, but volatile at the temperature of 212; and of a third substance, neither soluble in water nor volatile, but capable of combining with alkohol, or of being dissolved by it. These, mixed with each other, and attached to the insoluble ligneous fibre, formed the bark. In a similar manner, the seed or fruit of a vegetable, its juices, or any of its productions, may be analyzed.

The result of such researches is the discovery of a certain number of common principles, capable of being distinguished from each other by peculiar properties, and forming, by their mixture or combination, all the varieties of vegetable matter. It is to these chiefly that the attention of the chemist, so far as it is directed to the products of the vegetable kingdom, is confined. It would not only be an endless task to examine chemically every individual vegetable substance, but it would be one, in a chemical point of view, comparatively without utility, since many would be found so much alike, that no discrimination of them as chemical agents could be established. One essential oil, for example, may differ from another in its taste, or its odour, or in its action on the animal system; and similar differences may exist in different resins, or different gums. They are with propriety observed and recorded by the naturalist, or by the physician, as they are often adapted to important purposes in medicine or in the arts. But by the chemist, such trivial differences must be neglected. They probably depend, indeed, on variations in the chemical composition of the different substances; but such variations are by far too subtle to be traced with any accuracy by chemical analysis. Thus, the great number of essential oils which exist in the vegetable kingdom possess the same general chemical qualities, and would afford, on decomposition, the same ultimate principles in the same proportions; or, if any difference of proportion were observed, it could never be clearly established, that this was the cause of the differences in their properties. And the case would be the same with regard to the other proximate principles. This necessarily leads to a more general examination, or the chemist must rest satisfied with reducing all these varieties to a few well-defined species; those under each species agreeing in all their essential chemical properties and relations, though they may vary somewhat in their sensible qualities.

The first step, then, in the consideration of the vegetable substances, is the discrimination of these species, or of what are named the different Proximate Principles. These exist in the entire vegetable in various states. Some are collected in particular organs, nearly pure; others are mixed with the common sap, or with each other; and some are chemically combined together. Different methods, therefore, are employed to obtain them separate. Sometimes they are procured by spontaneous exudation from the living vegetable; some may be obtained by mechanical expression; those which are volatile are separated by the due application of heat, and others are extracted by their solubility in water, alkohol, or other solvents. When thus obtained separate, their properties are easily examined, and thus the requisite discriminations between them are established.

In the last place, it is necessary to investigate the composition of these substances. This is a subject of inquiry, however, extremely difficult: it is liable to all the inaccuracies arising from a complicated analysis; and we are altogether unable to bring our conclusions to the surer test which synthesis affords.

The first mode of effecting this analysis, and the one which has been most generally employed, is the mere application of heat. When a vegetable is raised to a temperature superior to 212°, in close vessels, the superfluous water it contains is first expelled: its decomposition then commences, and its elements enter into new combinations: a coloured empyreumatic oil distils over; this is accompanied and followed by an acid which condenses in the fluid form: a quantity of aërial fluid is also extricated, which, when examined, is found in general to be a mixture of carburetted hydrogen, carbonic oxide, and carbonic acid; and a quantity of charcoal remains, with minute portions of salts, earths, and metals, which the vegetable matter had contained. The nature of this analysis is sufficiently evident. The vegetable matter does not consist of the products thus obtained; but by the heat applied, the balance of attractions subsisting between its principles has been broken: these have entered into new combinations, and have formed the oil, the acid, and other substances which the analysis affords. The oil results from the union of part of the hydrogen with part of the carbon of the vegetable matter; the acid, from the combination of another portion of carbon and hydrogen with oxygen; and the carburetted hydrogen, and carbonic acid, are evidently other products of the same principles, united in other proportions.

This analysis of vegetables by fire was often performed by the older chemists. They supposed, that by means of it they might discover the source of the peculiar properties of different kinds of vegetable matter. With this view, above one thousand different plants were analyzed by the members of the French Academy, in the beginning of the last century, but with no advantage: the same products were afforded by the analysis of all of them; and these products not being such as pre-existed in the matter analyzed, but originating from new combinations of its principles, could give no just idea of its composition, at a time when these ultimate principles were entirely unknown.

Even modern chemistry derives limited information from such an analysis. We can indeed collect all the products, and we can farther analyze them, so as to determine their composition, or ascertain the simple substances of which they are formed, and the proportions in which they are united; and hence it might be concluded, that we might determine with certainty their absolute composition. But in such experiments, there are sources of error unavoidable, and nearly inappreciable. From slight variations of temperature, the new combinations formed will be considerably varied; and as the simple substances which thus act on each other are capable of combining in numerous modes and proportions, products will be formed whose composition we can scarcely exactly determine. We are also always uncertain what proportion of the products of the analysis have pre-existed in the vegetable matter, or have been actually formed. Thus, we can never know how much of the water it contained has been decomposed, or how much of the oil or acid obtained is the product of new combinations.

Still, from such an analysis, we derive some general information on the composition of the vegetable products; and several just and important conclusions from experiments of this kind are to be found in the works of modern chemists. If, for example, the vegetable substance which is exposed to heat yield a large quantity of acid, we conclude, that it has contained a considerable quantity of oxygen as a constituent part. It is thus that we discover that gum or sugar contains much more oxygen than the fixed or volatile oils do. If, again, it yield much oil, we conclude, that it contains a considerable quantity of hydrogen, since this element is the principal constituent part of empyreumatic oil. In like manner, when ammonia or prussic acid is afforded by this kind of analysis, we infer, that the substance operated on contains nitrogen, as that element is necessary for the formation of either of these substances. In the same manner, are discovered the earths and metals which the vegetable may contain; and from the quantity of charcoal which remains, we can draw some conclusion as to the quantity of carbon which had existed in its composition.

Sometimes the proximate principles of vegetables are analyzed by exposing them to heat, with the access of atmospheric air, and collecting the products of the combustion that takes place. From the nature of these products, we can ascertain the nature of its component principles; and from the quantities, we may even ascertain the proportions in which they were united. Oil, for example, when subjected to this analysis, yields nothing but carbonic acid and water. We conclude, therefore, that it is composed of carbon and hydrogen, since these principles united with oxygen form these products, and since, if any other simple substance had existed in the oil, it would have appeared, either pure, or in combination with oxygen. We can even determine in this manner the proportion in which the carbon and hydrogen existed in the oil. We know what quantity of carbon exists in a given quantity of carbonic acid, and what quantity of hydrogen exists in a given quantity of water; and therefore, by determining the quantities of carbonic acid and water produced by the combustion, we can ascertain the quantities of carbon and hydrogen which the substance contained. In this manner, Lavoisier found, that expressed oil consists of twelve parts of carbon united with three of hydrogen.

The proximate principles of vegetables are likewise sometimes analyzed by subjecting them to spontaneous decomposition. It is thus that sugar is brought into the state of fermentation; and from the products of the fermentation, the principles of the saccharine matter are determined. From such an operation, Lavoisier inferred, that sugar is composed of eight parts of hydrogen, twenty-eight of carbon, and sixty-four of oxygen.

Lastly, the analysis of these substances is effected by the agency of the acids, which communicate to them oxygen, and by the product the nature of their acidifiable base is ascertained. The nitric, and the oxymuriatic acid in particular, are employed with this intention.

Such, in general, are the methods by which vegetable matter may be analyzed. It is only necessary to observe, that experiments of this kind are subject to unavoidable errors in the execution, and that they afford little more than an approximation to the truth.

The following are the proximate principles of vegetables that have been discriminated with sufficient precision: Gum, Fecula, Sugar, Gluten, Albumen, Gelatin, Fixed Oil, Wax, Volatile Oil, Camphor, Resin, Extract, Caoutchouc, Tanin, Acids, Ligneous Fibre. To these have been added, some that are more equivocal, as the colouring matter, the aroma or spiritus rector, the bitter, acrid, and narcotic principles, and some others.

No uniformity is observed in the distribution of any of these principles, with regard to the different parts of plants. The ligneous fibre forms the basis of the entire vegetable; the others are distributed through every part; gum, for example, being found in the roots, bark, leaves, seed, and fruit, and the case being the same with nearly all the others. Gum, fecula, saccharine matter, and oil either fixed or volatile, generally form the matter of the seeds; the acids are usually contained in the fruit; the extractive matter is very generally diffused through the vegetable; tanin is found principally in the bark; the fixed oils are obtained in general either from the seeds or fruit, the volatile oils either from these, or from the wood, bark, or leaves. Gum, saccharine matter, and resin, often compose the secreted juices which spontaneously exude.

SECT. I.

OF GUM, OR MUCILAGE.

This principle of vegetable matter appears to be one of the first products of the changes to which the sap is subjected in the process of vegetation. It is contained in many plants; is found principally in the seeds and roots, but also in the stalks, bark, and leaves; and is sometimes formed in such quantity, as to be discharged by spontaneous exudation from the bark. It often exists in combination with some of the other proximate principles, particularly with fecula, sugar, extractive matter, and resin. There are seeds and roots, however, from which it can be extracted nearly pure, as from the seeds of the Linum usitatissimum, or the roots of Althea officinalis. When discharged by spontaneous exudation, it is generally pure; and from some of the gums obtained in this manner, its characters as a distinct principle are derived. When in a soft or liquid state, it is named Mucilage; when in a solid form, Gum.

Gum is generally in small fragments, wrinkled, and smooth on the surface, brittle, semi-pellucid, with frequently a tinge of yellow or red: it is inodorous and insipid: it is neither fusible nor volatile: when heated, it softens and blackens, and is soon decomposed: it has little inflammability; for although, when heated in contact with the air, its carbon or hydrogen may combine with oxygen, yet it scarcely presents the phenomena of combustion, the flame, even when the temperature is raised high, being scarcely perceptible.

Gum is soluble in water, either cold or warm, in every proportion. Its solution is viscid, and, when the proportion of gum is considerable, is of a thick consistence, and is adhesive. By evaporation, the gum may be obtained in a concrete form, and is soluble in water as before.

The solution of gum in water becomes sour on being kept for some time, from the formation of a portion of acetic acid. This change is said to arise merely from the re-action of its own elements, and not from the absorption of oxygen. By no management can gum be made to undergo the vinous fermentation. When mixed with yeast, and kept in the proper temperature, it retains its natural taste, and acquires, after a number of days, only a peculiar and offensive smell *.

Gum is perfectly insoluble in alkohol. This re agent even precipitates it from its watery solution, or rather renders the solution milky, and is the test by which gum

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* Cruickshank in Rollo on Diabetes, p. 471.

is usually recognised. It is also insoluble in ether, and in oils, either volatile or fixed. From its viscosity, mucilage serves to diffuse oil more perfectly through water, and to retain it in this state of diffusion, forming a milky mixture; and for this purpose it is employed in pharmacy.

Gum is not directly dissolved by any of the concentrated acids, but is decomposed by them, the decomposition varying as to its products, according to the kind of acid, and according to its state of concentration. Sulphuric acid blackens it, or evolves a quantity of its carbon: it causes, at the same time, part of its oxygen and hydrogen to combine to form water; and a portion of acetic acid is also produced.

Nitric acid exerts a different action upon it. No carbonaceous matter is separated; but the elements of the gum receive oxygen from the nitric acid, and portions of oxalic acid, malic acid, and the peculiar acid named saccho-lactic, are formed. The products, however, appear to be different, according to the concentration or dilution of the nitric acid, and according as its action on the gum is promoted or not by heat. Mr Cruickshank appears, by using a diluted acid, to have obtained from gum only oxalic acid, a small portion of oxalate of lime being likewise deposited from part of the acid combining with the portion of lime which is always contained in gum. From treating an ounce of gum arabic with an equal proportion of nitric acid properly diluted, the quantity of crystals of oxalic acid formed amounted to 3 drachms 36 grains. With these were mixed a white powder, amounting to about 6 grains, which he found to be oxalate of lime; nor does any saccho-lactic acid appear to have been formed *.

On the other hand, from the experiments of Fourcroy and Vauquelin, it appears, that the quantity of this acid, produced by the action of nitric acid on gum, is considerable, when the nitric acid is concentrated, and its action promoted by heat. In this mode of making the experiment, from 14 to 26 parts of saccho-lactic acid were obtained from 100 parts of gum. If the acid has not been boiled on the gum, or if it has not been concentrated or employed in too large quantity, malic acid is also formed with the oxalic acid, and it is converted into this latter acid, by the continued action of the nitric acid. From 100 parts of gum arabic, these chemists obtained 24 of malic acid, care being taken to avoid the conversion of any of it into oxalic acid †.

Oxy-muriatic acid converts gum principally into citric acid. For this purpose, it requires to be applied in its concentrated state, a current of oxy-muriatic acid gas being transmitted through a solution of gum in water. Vauquelin, who made this experiment, found that the gum was almost entirely converted into citric acid ‡. Muriatic acid exerts little action on gum. It may be dissolved in the concentrated acid; the liquid becomes brown; a little carbon is separated; the gum is changed in its properties, but does not appear to be converted into any acid.

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* Rollo on Diabetes, p. 468.

† Fourcroy's System of Chemistry, vol. vii. p. 197, &c.

‡ Annales de Chimie, tom. vi. p. 178.

The alkalis and alkaline earths, when dissolved in water, dissolve gum without producing on it much change.

The decomposition of gum by heat affords that mode of analysis by which we discover with most accuracy its elements and their proportions. The products are a large quantity of an acid liquid formerly regarded as a peculiar one, and named, as being obtained from the decomposition of mucilage by fire, pyro-mucous acid, but now discovered to be acetic acid, disguised a little by a small portion of empyreumatic oil: With this acid liquor, there distils also a portion of empyreumatic oil; carbonic acid gas and carburetted hydrogen gas are produced, and there is a residuum of charcoal, light and spongy. From this analysis, it was inferred, that gum consists of carbon, hydrogen, and oxygen, these being the elements of these products. The quantity of acid being greater than that of oil, it was inferred, that gum contained more oxygen than some of the other vegetable principles; while, being less than that from sugar, it was supposed to differ from this principle, in containing a smaller proportion of oxygen. The proportions, as given by Fourcroy and Vauquelin, were 23.08 of carbon, 11.54 of hydrogen, and 65.38 of oxygen. The experiments of Mr Cruickshank have thrown more light on its composition. He observed, that when the pyro-mucous acid obtained in its analysis by heat, was saturated with lime, a strong smell of ammonia was perceptible; hence this alkali had been formed in the decomposition of the gum, and of course nitrogen must enter into the composition of this substance. He farther found, that the residual charcoal contained a little lime, in part combined with phosphoric acid. From one ounce of gum arabic exposed to heat in a retort, there were obtained 3 drachms and 30 grains of pyro-mucous acid, diluted with water, and mixed with a little empyreumatic oil; the residuum of charcoal amounted to 1 drachm 46 grains; 273 ounce measures of aërial fluid were collected in the apparatus connected with the retort, of which 93 were carbonic acid, and the remaining 180 that variety of carburetted hydrogen that is obtained from moistened charcoal by exposure to heat. The charcoal, when burnt, left a whitish powder, amounting to about 10 grains, which was found to be lime, mixed with a very small portion of calcareous phosphate. Similar results were obtained from gum tragacanth, another pure gum; one ounce of it yielded 4 drachms 5 grains of pyro-mucous acid, 1 drachm 45 grains of charcoal, 78 ounce measures of carbonic acid gas, and 91 ounce measures of carburetted hydrogen gas. The acid, when supersaturated with lime, gave out still more ammonia than was disengaged from the acid obtained in the decomposition of gum arabic; and the charcoal, when burnt, left a white residuum of 12 grains, which was found to consist of lime, with a little calcareous phosphate. Lime was also discovered by re-agents in the solution of gum arabic in water: when a small quantity of sulphuric acid was dropped into it, needle-like crystals were slowly deposited; and when these were redissolved in distilled water, and oxalate of ammonia added, a copious precipitate of oxalate of lime immediately took place *.

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* Rollo on Diabetes, p. 462. 465.

Vauquelin has since given some additional facts on the analysis of gum. He not only found carbonate of lime, with a small proportion of phosphate of lime in the ashes left after the combustion of gum, but likewise a small quantity of oxide of iron. The lime existing in gum, he supposes to be combined with an acid; as the solutions of gum, instead of giving any indications of pure lime, rather indicate acidity; and a bit of gum, rubbed on paper moistened with a blue vegetable juice, rendered it red. The only soluble compounds of lime with a vegetable acid are those with the malic and with the acetic. The former is only soluble with an excess of acid; it is probable, therefore, that it is with the acetic acid that it is combined,—a probability confirmed by the consideration, that acetic acid exists in the sap of vegetables of which gum appears to be one of the first products *.

From the experiments on the composition of gum, it follows, that its ultimate elements are carbon, hydrogen, and oxygen, the proportion of oxygen being less than in saccharine matter; but that with these are also combined smaller proportions of nitrogen and lime. From the addition of these last elements, an important difference is established between gum and other two principles with which it has some relations, fecula and sugar: they are capable of being made to pass into the vinous fermentation, which gum is not; and this difference appears to be owing to their presence, principally, perhaps, to that of the lime. Mr Cruickshank accordingly found, that when

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* Nicholson's Journal, vol. xii. p. 256.

lime was added to a solution of sugar, the latter was rendered incapable of undergoing the fermentative process *.

Gum is usually obtained, either by spontaneous exudation, or by incisions made in the trunk and branches of trees. Its existence in vegetables is easily detected. It is only necessary to boil gently the vegetable substance with water: the water dissolves the gum; and if the vegetable contained much of it, the decoction will be glutinous. It may be allowed to stand till the impurities have subsided: it is then to be evaporated to the consistence of thin syrup. The addition of three parts of alkohol will precipitate the gum.

Of the different gums, those obtained by spontaneous exudation are the purest, though they also differ in purity, and in some of their qualities, as produced from different plants. The purest of them, the Gum Arabic, is the produce of the Mimosa nilotica, a plant a native of Egypt and Arabia. It is white or yellowish, semi-transparent and brittle, perfectly insipid, and free of odour. It is easily soluble in water, forming a viscid solution. Gums exude from the cherry, plum, and other trees of this country, very similar in their qualities to the gum arabic, but less pure, and more coloured.

The other principal gum, termed Tragacanth, is the produce of the Astragalus tragacantha, a native of the island of Crete. It is in small wrinkled pieces, less brittle and less transparent than those of the other gums. Its solution in water is much more viscid and adhesive than that of the gum arabic. It is also somewhat opaque, and

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* Rollo on Diabetes, p. 471.

does not feel glutinous, but slippery. From this circumstance, Hermbstaedt has distinguished these two substances as different proximate principles, applying the name of Gum to that which forms with water a transparent glutinous solution, and that of Mucilage to that which forms with water a solution more or less opaque and slippery; gum arabic being given as an example of the one, tragacanth of the other *. This distinction, however, is entirely nugatory. The slight cloudiness of the solution of tragacanth, or of the mucilages of seeds or roots, may be owing to the admixture of a minute portion of fecula, oil, or some other vegetable matter. In all their essential properties they are perfectly alike; and Mr Cruickshank's experiments show, that their composition is the same.

It appears, that, from some of the vegetables of this country, gum or mucilage may be extracted in such quantity, that they may afford a source whence an abundant supply may be derived for its consumption in some of the arts, particularly in calico-printing, in which it is largely used. Mr Willis some years ago observed, that the root of the plant called blue-bells or hare-bells (Hyacinthus non-scriptus) was extremely mucilaginous. A pound of the bulbs of this root, when dried, yielded about four ounces of a powder which afford to water, by maceration, a strong mucilage, and, when tried for the purpose of thickening the mordant and fixing the colours in calico-printing, was found to answer equally well with gum arabic, when used in the same proportion †. He

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* Medical and Physical Journal, vol. i. p. 75.

† Nicholson's Journal, 8vo. vol. vii. p. 30.

has since discovered other vegetables, the roots of which afford a mucilage equally strong with that of the Hyacinthus non-scriptus, particularly the vernal squil (Scilla verna) and the white lily, (Lilium candidum), and which might be used as substitutes for gum arabic when it bears a high price *. Some experiments on the mucilage of the Hyacinthus non-scriptus, and on its application to useful purposes, have been likewise made by Leroux. He has given different methods of preparing it: that which on the whole answers best, is to macerate the bulbs of the root in a sufficient quantity of water, to form a thick mucilage, which is expressed, and dried by exposure to the air. This mucilaginous matter appears, from his experiments, to have all the properties of gum: it afforded the same products by analysis, and suffered similar changes from the action of the acids †.

A discovery of perhaps still more importance in the arts, is that of a method of extracting a mucilage, which may be employed as a substitute for gum, from the different lichens which grow on the bark of our common trees and shrubs. The method was discovered and made public by Lord Dundonald ‡. "The lichen does not consist entirely of a gummy matter. There is the outer skin or cuticle; below that a green resinous matter; the remainder of the plant consists of partly gum, partly a matter somewhat analogous to animal substances, and a

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* Nicholson's Journal, 8vo. vol. ix. p. 234.

† Annales de Chimie, tom. xl. p. 145.

‡ Philosophical Magazine, vol. x. p. 293.

small proportion of fibrous matter, which cannot be dissolved by boiling, or the action of alkaline salts.

"The first process in preparing gum from the lichen is to free it of the outer skin of the plant and the resinous matter. This is done by scalding the lichen two or three times with boiling water, allowing it to remain so long in the water as, by absorbing it, to swell: in doing this, the skincracks, and comes off along with the greatest part of the resinous matter. Or it may be freed from them by gently boiling the lichen for about fifteen or twenty minutes, then washing it in cold water, laying it afterwards upon a stone or brick floor, where it should lie for ten or twelve hours, or perhaps more. The reason for this is, that the exposure for that time to air greatly facilitates the subsequent extraction of the gum.

"The scalded lichen is then to be put into a copper boiler with a due proportion of water, two wine gallons to every pound of lichen, and boiled during four or five hours, adding about half an ounce or three quarters of an ounce of soda or pearl-ashes for every pound of lichen; or, instead of these salts, about half an English pint of volatile alkali. The boiling should be continued until the liquor acquires a considerable degree of gummy consistence. It is then to be taken out of the boiler, allowed to drain through a wire or hair cloth. The residuum is to be put into a hair cloth bag, and to be squeezed in a press similar to that which is used by the melters or rinders of tallow.

"The first boiling does not extract the whole of the gum. The lichen should be boiled a second and even a third time, repeating the process as above described, diminishing at each process the quantity of water and the quantity of alkali, which a little experience will soon point out. When three boilings are employed, the gummy extract of the last boiling should be kept for the first boiling of a fresh batch of lichen. The extract proceeding from the first and second boilings should be mixed together, and evaporated to the consistence necessary for block or press printing. The evaporating vessels should be of tin or thin lead, placed over a range of stoves, and moderately heated by fire or the steam of water."—"When gum from the lichen is to be employed for making ink, manufacturing and staining paper, and for stiffening silks, crapes, and gauzes, it should be extracted from the lichen without employing any alkaline salts, continuing the boiling or digestion longer, and with a moderate degree of heat, in which case the gummy extract will be nearly colourless. When volatile alkali is used, the boiler should be of iron, as volatile alkali acts on copper." From a calculation which Lord Dundonald adds, it appears, that the mucilage thus obtained may be used with much advantage as a substitute for gum; and it has, I believe, been employed by the calico-printers of this country, at least in some of their processes.

Pure gum is not an active substance, considered with respect to its effects on the living system. In medicine, it is only used for its lubricating quality; and so little activity does it exert, that it has often been taken for a considerable time as an article of food. Though pure gum, however, is thus inactive, the virtues of many vegetables are found to depend on a gummy matter.

From its chemical properties, gum is of rather more importance. As a component part of vegetable matter, it renders the other parts more soluble in watery liquors. In pharmacy, it is often used as a medium to suspend oils, balsams, and resins, in water. In the arts, the different gums are applied to various purposes, from their adhesive quality, and to diffuse powders in watery fluids: they are thus used in dying, ink-making, calico-printing, &c.

SECT. II.

FECULA, OR STARCH.

The term Fecula, or Starch, is appropriated to a substance existing in vegetables, similar in many of its properties to gum. It is a dry, white, insipid powder, which forms the principal part of the nutritive grains and roots. It is extracted from them by beating them in water, or by working the powder of them, made into a paste with water, in the hand: the soluble parts are dissolved; the fibrous and glutinous parts remain unaltered; and there is diffused through the water a fine white powder, which gradually subsides, and may be dried. This is termed the Fecula of the plant.

If wheat flour, for example, be subjected to this operation,—if a quantity of it is made into a paste with water, inclosed in a bag, and wrought constantly, while a stream of water is poured upon it, the greater part of it is carried off in the form of a white powder, which forms the substance commonly named Starch. This is a pure fecula. A similar product may be obtained from rye, and, in general, all those grains which are used as food. It can also be obtained from the potatoe, and from other roots and stems of plants. Sometimes it is extracted from the most poisonous or acrid plants, the poisonous or acrid matter being soluble in the water, and being, of course, easily separated from the fecula.

The principal of these is the starch of wheat, which is prepared in the following manner: The grain, well cleaned, is kept in cold water until it soften and swell, so that the husk separates; and by pressure, it then gives out a milky fluid. The grains are put into a hempen bag, and pressed or beat, cold water being poured on them in sufficient quantity. The fecula is thus pressed out, and diffused through the water. As the water receives from the grain at the same time a quantity of saccharine matter, it soon runs, in the temperature at which it is kept, into the acetous fermentation; and the weak acid thus formed, by digesting on the fecula, renders it much whiter than it otherwise would be. After it has subsided, the clear liquor is run off; the precipitate is repeatedly washed with water; it is then pressed in a cloth to force out the water; is cut into small pieces, and dried with a moderate heat.

When, by any process of this kind, a fecula is obtained pure, it exists under the form of a light white powder, easily divisible, and very soft to the touch, and when surveyed in a strong light, appearing to be in the state of minute brilliant grains; it is insipid, and inodorous. Sometimes it remains still united with some of the other principles of the plant, from which it receives more or less colour, smell, and taste. Fixed oil, when united with it, is separated perfectly with difficulty; and a compound of this kind forms the residuum obtained in the extraction of fixed oil by expression from seeds.

The peculiar property by which this principle is clearly distinguished from every other, is its complete insolubility in cold water, while with hot water it forms a gelatinous solution. Its insolubility in cold water is very evidently shown in the mode in which it is prepared, as, although it is agitated in the water, and suspended in a state of very minute division, no part of it is dissolved. Its solubility in hot water is discovered, by diffusing a little of it in cold water, and heating the mixture to a temperature of 160 or 180, or by pouring boiling water on it. In either case, a solution of it takes place, more or less gelatinous, according to the proportion of water employed. This jelly may be dried into a stiff hard mass, which is still insoluble in cold, soluble in hot water.

By forming a gelatinous solution in hot water, fecula appears to approach to the nature of gum; but its total insolubility in cold water at once distinguishes between them, and characterizes it as a peculiar principle.

There is another chemical quality by which it is not less unequivocally distinguished; it is capable of being converted into sugar, and of thence passing into the vinous fermentation, which neither gum nor any of the other vegetable principles is.

Fecula is entirely insoluble in alkohol, or in ether.

Exposed to heat in contact with the air, it blackens, swells up, and forms a spongy charcoal. If strongly heated, it burns. When heated in close vessels, it affords a large quantity of dilute pyro-mucous or acetic acid, with a little empyreumatic oil; carbonic acid and carburetted hydrogen gases are extricated, and a portion of charcoal remains. From this analysis, fecula appears to be a ternary compound of carbon, hydrogen, and oxygen. Some traces of phosphate of lime are to be found in its ashes; but this may arise from the gluten often associated with fecula, a small portion of which may adhere to it.

The action of the acids on fecula is somewhat analogous to that which they exert on gum. When much diluted with water, they dissolve it, especially if the temperature be raised, and form a gelatinous solution. If concentrated, they decompose it. Sulphuric acid blackens it, by evolving a portion of charcoal; and water and acetic acid are at the same time formed. The action of muriatic acid is similar, but less energetic. Nitric acid does not separate its carbon in a sensible form, but affording to it oxygen, converts it into malic and oxalic acids. This action takes place most completely when the nitric acid is a little diluted, and a moderate heat applied.

The alkalis, when in solution in water, dissolve fecula or reduce it to the consistence of a jelly, without the assistance of heat. The acids separate it from this combination.

There are few plants which do not afford more or less of this principle; and it is contained in all the nutritive seeds and roots. It is generally mixed or combined with other principles, and sometimes intimately, so as not to be easily separated. It does not appear to be completely formed but in certain states of vegetation. Thus, in the nutritive grains, it is perfect only when they have attained maturity: previous to that period, it is in a state approaching to mucilage mixed with saccharine matter. It is probably formed from mucilage in the progress of vegetation; and Leroux, in his experiments on the mucilage of some of the tuberose roots, observed, that in the mere drying of the mucilage, especially towards the end of the process, when the matter began to lose its humidity, a portion of it appeared to be converted into fecula *.

This principle is sometimes employed in its pure state medicinally, from its nutritious quality, and from being easy of digestion. Sago and salop are fecula of this kind. The former is the produce of the Cycas circinalis, and is extracted from the pith of the stem and branches, by maceration in water: it is washed, passed through a perforated copper plate, so as to reduce it to grains, which are dried. Salop is the produce of the Orchis mascula. The lately introduced arrow-root powder is said to be the produce of the Maranta arundinacea. Cassava is prepared from the tuberose root of the manioc, (Jatropha Manihot). With the fecula of this root, there is associated an acrid and poisonous juice, which is however completely separated by washing, in the process by which it is extracted. The roots of the Bryonia alba and the Arum maculatum are likewise composed principally of fecula, associated with acrid matter, which is separated in the process by which the fecula is extracted from them. These two were formerly prepared for medicinal use. Wheat affords perhaps a larger quantity of fecula than any other vegetable substance, and in a state of perfect purity. A very pure

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* Annales de Chimie, tom. xl. p. 156.

fecula, in large quantity, is also extracted from the potatoe, the root being peeled, well cleaned and rasped, the pulp placed on a hair sieve, and water poured on it until the fecula is extracted, which, after being deposited, is washed and dried. It amounts, according to Dr Pearson's experiments, to from 15 to 17 parts in 100 of the root, the remaining parts being water, with 8 or 9 of fibrous matter, and 5 or 6 of mucilage *: this fecula has been used as a substitute, in stiffening linen, and similar purposes, for the starch of wheat. Lastly, some of the lichens contain a large quantity of fecula; and the Lichen islandicus, which has been celebrated for its mild nutritive quality, consists entirely of it, so as to afford a fecula nearly pure, when reduced to powder.

Fecula is, of any variety of vegetable matter, best adapted to the nourishment of animals; and it forms the principal part of all the seeds and roots which are used as articles of food by man. Its high nutritious power is well shown, by the fact, that some of the most nutritive of these, and which even alone are capable of sustaining animal strength and growth, as rice, or the potatoe root, contain no other principle that can contribute to this, but fecula. Thus, the root of the potatoe, according to Dr Pearson's analysis of it, contains, besides fecula, only a small portion of mucilage and fibrous matter; yet, as he remarks, "there is sufficient evidence, that the potatoe root and water, with common salt or other seasoning, can nourish as well as any other vegetable matter and water, with seasoning.".

Fecula, besides its use, either pure, or under the form

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* Repertory of Arts, vol. iii. p. 389.

of the nutritive grains as an article of diet, is used in the state of its gelatinous solution, for pasting and stiffening linen or other kinds of cloth. It also enters into the composition of some pigments.

Rose has lately pointed out a principle very analogous to fecula, though differing from it in some properties, which is extracted from the root of elecampane, (Inula helenium). It is deposited in the form of a white powder from the decoction of the root, after it has stood for some hours. It is insoluble in cold water; is soluble in boiling water: the solution, though liquid while hot, becomes gelatinous as it cools; and in the course of some hours, the solution deposites the greater part of the substance dissolved, in the form of a compact white powder. Alkohol precipitates it from its solution in water. This white matter, thrown on burning fuel, melts like sugar, and evaporates, diffusing a white pungent smoke, leaving a small coally residuum. At a red heat, it burns with a vivid white flame. By distillation, it gives an empyreumatic acid, without any empyreumatic oil. Nitric acid converts it into malic and oxalic acids, and, when in excess, into acetic acid From these properties, it is inferred by Rose, that this substance is neither gum nor fecula, but intermediate between them; and he considers it as probable, that several products, which have been regarded as varieties of fecula, are rather of the nature of this powder *.

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* Nicholson's Journal, vol. xii. p. 97.

SECT. III.

SUGAR.

SACCHARINE matter is very generally mixed with the fecula in the seeds and roots of vegetables. It exists also in still larger quantity as one of the secreted or proper juices of the plant. It is not a constant principle, but is formed chiefly, or in any considerable quantity, only at certain periods of vegetation. In fruits, it is found in abundance only in a state of maturity; and in those plants which afford it in largest quantity, it is more abundant at certain periods than at others.

The plant named the Sugar Cane (Arundo saccharifera) has been long cultivated for the production of sugar. The juice of it, at a certain season, consists principally of saccharine matter: it is pressed out by subjecting the canes, cut short, and tied in bundles, to the pressure of three upright iron rollers or cylinders, the middle one of which is made to revolve. The expressed juice is immediately conveyed into copper pans, in which it is to be clarified. This is done by heating it with a quantity of pure quicklime, by which the portion of acid present in the juice, and which prevents the concretion of the sugar, is neutralized; the lime in combination with this acid, and with some other vegetable matter, is precipitated: towards the end of the operation, a scum collects on the surface, consisting of the mucilaginous and oily matter of the juices, with any grosser impurities entangled in it.

When this is fully formed, the fire is damped, and the liquid is allowed to remain at rest, to become clear. It is afterwards run into the evaporating boiler, in which it is made to boil, the scum, as it rises to the surface, being removed: it is removed from one evaporating vessel into another, as the evaporation proceeds, until it be so far boiled down, that on cooling, the sugar will concrete. It is then run into the cooler, a large shallow wooden vessel, in which this operation takes place; and from the concrete sugar, the remaining liquid part, the Molasses of commerce, is drained off.

The sugar thus obtained is in the state of small crystalline grains, of a brown colour, and is not perfectly pure. It is sometimes obtained in a purer state, by running the inspissated juice into vessels of a conical form, the apex of the one being undermost, in which it is allowed to concrete; by an aperture at the bottom, the remaining liquid is withdrawn, and there is applied to the base of the cone, or the uppermost part in its inverted position, a layer of clay, which is kept moist with water: this water filtrates slowly through the sugar, and more completely removes the molasses.

In Europe, the sugar is purified by a process somewhat similar. It is dissolved in lime-water, and boiled, the lime being supposed to neutralize a small portion of acid that is still present in the unrefined sugar: a quantity of blood is added, which forms a coagulum during the boiling, that rises to the surface, and entangles the impurities. The clear liquor is boiled down to the proper consistence: it is run, when cold, into conical clay moulds, which are placed with the apex of the cone undermost: when it has become concrete, an aperture is made at this point; the base of the cone is covered with clay, which is moistened with water; and this water, slowly transuding through the sugar, dilutes and removes any superfluous syrup: the conical loaves are then dried in a stove. This operation is even sometimes repeated: the sugar is thus brought to the state of greatest purity: it is in the form of a mass, composed of crystalline grains, white, and having a taste perfectly sweet, without any peculiar flavour.

Other plants besides the sugar cane produce saccharine matter in such abundance, that it is extracted from them. In America, large quantities are obtained from the sugar maple, (Acer saccharinum). According to the account of the mode of extracting it given by Dr Rush, the saccharine juice is most abundant in the tree in the spring months: the stem of the tree is at that season bored with an auger, the instrument being introduced about three-fourths of an inch, and in an ascending direction, and the aperture being afterwards deepened gradually to the extent of two inches. When the juice ceases to flow from this, or is much diminished in quantity, a similar aperture is made in another part; and in the course of from four to six weeks, during which the juice continues to flow, a large quantity is collected. The saccharine matter is procured from it by boiling it until the greater part of the superfluous water is dissipated; a small quantity of slacked lime being added, with a portion of milk, or of the whites of egg to clarify it, and a little butter, to prevent the liquor from boiling over the vessel. The sugar is made to concrete, and is clayed and refined nearly in the same manner as is practised in the manufacture of sugar from the sugar cane. From the juice yielded by a tree of the usual size, five pounds of sugar may be extracted, and the operation can be repeated annually, the tree not being injured by the tapping *. The tree begins to afford the saccharine juice when twenty years old, and ceases to afford it when about sixty or seventy years of age.

The beet (Beta vulgaris), the parsnip (Pastinaca sativa), the carrot (Daucus carotta), the turnip (Brassica rapa), and several other plants allied to these in their natural characters, are known to contain, at certain periods of their growth, juices possessed of a considerable degree of sweetness, deposited principally in their roots; and Margraaf long ago extracted from all of them a portion of sugar †. A few years ago, the production of sugar from the beet engaged in particular the attention of the German chemists; and it was supposed, that it might be cultivated with advantage, to obtain a substitute for the sugar of the West India islands. Different memoirs on this subject have been published by Achard ‡, Hermbstaedt ||, Lampadius ¶, and others. The general process for extracting it, as described by Achard §, consists in softening

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* Transactions of the American Philosophical Society, vol. iii. p. 64.

† Mémoires de l'Acad. des Sciences de Berlin, 1747.

‡ Nicholson's Journal, 4to, vol. iii. p. 237. 288.

|| Ibid. p. 333. 410.

¶ Annales de Chimie, tom. xxxviii. p. 76.

§ Ibid. tom. xxxii. p. 264.

the roots, by boiling in water, cutting them in slices, and expressing the juice by a press. The expressed juice is strained, and is reduced by boiling to about two-thirds. It is then strained, and is reduced, by farther boiling in a smaller boiler, to about one-half. It is strained a third time, and, in a still smaller boiler, is reduced to the consistence of a syrup. This syrup, put into shallow earthen vessels, is kept in an apartment heated by a stove to a temperature of from 80 to 120 of Fahrenheit, until the sugar is deposited in an irregular crystallized mass. The remaining liquid is poured off, and the soft mass of sugar is subjected to pressure, gradually increased, in a bag, so as to force out the liquid part, and obtain the sugar dry. The addition of a portion of lime-water in the boiling has been supposed to facilitate the concretion of the sugar, and has, in particular, been recommended by Lampadius, and supposed by him to operate by neutralizing the acid contained in the juice. He has introduced some other variations in the process, as expressing the juice from the roots without previous boiling, adding in the subsequent boiling a portion of milk, which, by its coagulation, serves to clarify the juice; and reducing the heat considerably in the last stage of the evaporation *. And Achard, in a process which he has given subsequent to the first he proposed, employs a little sulphuric acid to coagulate the albumen of the juice, and afterwards lime, both to abstract this acid, and promote the crystallization of the sugar †. More lately, Hermbstaedt has

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* Annales de Chimie, tom. xxxviii. p. 76.

† Nicholson's Journal, vol. xii. p. 259.

given a process still more simple, and less expensive. The juice of the beet being expressed, is clarified with lime, in the same manner as the juice of the sugar cane. It is then evaporated to the consistence of syrup, is left to cool, when a coarse brown sugar concretes, leaving a portion of syrup *.

In some former experiments, Hermbstaedt obtained, from 125 lbs. of the roots of the Beta vulgaris, $5\frac{1}{3}$ lb. of brown sugar, and $1\frac{7}{8}$ lb. of syrup, which drained off. This sugar has rather a disagreeable taste, but by clarifying the juice with the white of an egg, (for which, in the large way, blood might be advantageously substituted), the sugar is obtained white and pure †; and by some process of this kind, it has been manufactured and refined so as to be equal to the common refined sugar ‡. The product, however, is very various, and is much dependent, as Achard has shown, on the methods practised in the cultivation of the plant; and by a due attention to those circumstances by which the production of saccharine matter is increased, he calculated, from his experiments, that in Germany brown sugar might be obtained from the beet in the large way, at an expence not exceeding threepence *per* pound. In a report presented to the National Institute, the result of the calculation is rather less favourable; but the reporter admits, that the experiments on which this was founded were not sufficiently varied, nor on a large scale ||.

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* Nicholson's Journal, 8vo, vol. xiii. p. 267.

† Ibid. 4to, vol. iii. p. 168.

‡ Ibid. p. 474.

|| Ibid. tom. xxxv. p. 134.

The fecula of vegetables, it has already been remarked, is convertible into saccharine matter by the action of oxygen. This takes place in germination, and when performed on grain previous to fermentation, constitutes the process of malting.

Sugar is also produced in the animal system in some morbid states, and is discharged by some of the secretions in considerable quantity.

Sugar, when pure, has a perfectly sweet taste, free from any peculiar flavour: it is inodorous and of a white colour; and in the state in which it is usually prepared, is in masses composed of brilliant grains: the sugar from different vegetables, however, often retains a portion of extractive, mucilaginous, or oily, matter, from which it derives taste, flavour, and other qualities.

Sugar is abundantly soluble in water: at the temperature of 50 it does not require more than its own weight for its solution. At a higher temperature the quantity dissolved is greater; and at that of 212 the water can retain any quantity in solution. The consistence of a strong solution of sugar in water, is thick and viscid. In pharmacy it is named Syrup, and different syrups are prepared from vegetable juices, or vegetable infusions, by an addition of the requisite proportion of sugar.

Sugar crystallizes from its saturated solution: the form of the crystals is a prism of four or six sides, bevelled at each extremity, or sometimes acuminated by three planes *.

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* Journal de Physique, tom. xliii. p. 462.

Sugar is likewise soluble in alkohol, and the solution affords crystals on evaporation. In the vegetable analysis, this solution may be advantageously employed to extract sugar from those vegetable products which contain it in small quantity, as it frees it from the mucilage which otherwise adheres to it; and by slow crystallization it may be separated from any other principle which the alkohol had dissolved. By this process Margraaf obtained pure sugar from a number of vegetables.

When exposed to heat sugar is blackened, swells up, and burns to a coal; and if the heat be high this is accompanied with flame. The products of its combustion are water and carbonic acid.

The fixed alkalis combine with sugar in solution in water: the alkaline properties, as Lowitz observed, are little altered by the combination, even when a large quantity of sugar is used, and the alkali is boiled with it. The sweet taste of the sugar is nearly destroyed, but on adding sulphuric acid, and precipitating the sulphate by alkohol, the sweetness is completely restored [*]. The compound of sugar and potassa appears not to be soluble in alkohol, though both its ingredients are: Mr Cruickshank having found, that when alkohol was added to a portion of the solution of sugar and pure potassa, after it had been boiled to the consistence of a syrup, no union took place, but the alkohol, though the mixture was repeatedly agitated, swam on the surface.

The action of the alkaline earths on sugar is similar to that of the alkalis. In boiling a solution of sugar with a little lime, Mr Cruickshank found, that the lime combined with the sugar, and communicated to it a very bitter astringent taste, though the sweetness still in some degree remained : by evaporation the liquid was reduced to a semi-transparent substance, much more tenacious than the thickest syrup, and having a rough bitter taste mixed with a certain degree of sweetness. On adding alkohol to the original solution, a precipitate in white flakes was formed, which appeared to be a combination of sugar with lime. Sulphuric acid added to the solution, precipitated the lime in the state of sulphate, and in a great measure restored the natural taste*. Lowitz had before observed, that sugar communicates a much greater degree of solubility to lime, equal parts of them being boiled together in water. In reducing this compound to dryness by inspissation, a white mass was obtained extremely acrid and caustic. The solution in boiling, he found to become thick and turbid, lime being precipitated; but as it cools the lime is redissolved, and it recovers its transparency. Alkohol added to it, precipitates the lime; the alkaline carbonates decompose it by forming carbonate of lime; and it appears to be decomposed on exposure to the air, from absorption of carbonic acid, minute crystals being formed, and the sweetness of the sugar being at length restored †.

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[*] Cruickshank, Rollo on Diabetes, p. 461.

Sugar is decomposed by the acids. Sulphuric acid blackens it, by causing an evolution of part of its carbon in the state of charcoal, while the remaining principles of the sugar enter into new combinations, forming a portion of water, and probably of some of the vegetable acids. Nitric acid yields oxygen to it, and converts it into an acid, which, from being abundantly formed by this oxygenizement of sugar, was at one time named Saccharine acid, and which Scheele demonstrated to be merely oxalic acid. The process consists in pouring six parts of nitric acid on one part of sugar in coarse powder, and applying a moderate heat; an effervescence takes place, and nitrous acid vapour is disengaged: the application of the heat is continued until this ceases, and in the remaining liquid prismatic crystals soon begin to form, which consist of oxalic acid, and which, according to Mr Cruickshank's experiments, amount to rather more than half the weight of the sugar. There remains an uncrystallizable liquid, consisting principally of malic acid. The action of oxymuriatic acid on sugar, is somewhat different as to its results. According to the observation of Vauquelin, when a little sugar is put into liquid oxymuriatic acid, it is converted into citric acid; but if oxymuriatic acid gas be transmitted through a solution of sugar, the liquid when evaporated affords a residuum, presenting all the characters of caramel or sugar that has been imperfectly burnt *.

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* Rollo on Diabetes, p. 461.

† Journal de Physique, tom. xlii. p. 460.

From the chemical changes which sugar suffers from the preceding re-agents, it may be inferred, that it is a compound of carbon, hydrogen, and oxygen. Its composition is however determined with still more precision, by its decomposition by heat. The products of its destructive distillation in close vessels, are an acid liquor, be-

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* Annales de Chimie, tom. vi. p. 220.

ing acetic acid diluted with water, and a little empyreumatic oil ; carbonic acid, and carburetted hydrogen gases, are disengaged in considerable quantity; and the residuum is charcoal. The proportion of acid is larger than that obtained from the decomposition of gum. From one ounce of sugar decomposed by heat, the products in an experiment made by Mr Cruickshank * were

	Dr.	*Gr.*
Acid with a drop or two of empyreumatic oil,	4	30
Charcoal, - - - - -	2	0
Carburetted hydrogen gas, -	119 oz. measures.	
Carbonic acid gas, - -	41 — ———	

The acid, when saturated with lime, gave no indication of ammonia, as that from gum does ; neither did the charcoal contain any lime : neither nitrogen nor lime therefore enters into the composition of sugar, and it is to be regarded as a compound merely of carbon, hydrogen, and oxygen. It differs from gum in the absence of nitrogen and lime ; and from fecula probably in the proportion of oxygen being larger and of carbon being less ; since in the process by which fecula is converted into sugar, oxygen is absorbed and carbonic acid evolved. The proportions of its principles, as determined by Lavoisier, from the changes it suffers in the process of fermentation, are 64 of oxygen, 28 of carbon, and 8 of hydrogen ; but these were inferred from results so complicated, that they cannot be regarded as at all certain.

From the differences which exist in the composition of gum, fecula, and sugar, we may trace, though perhaps in

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* Rollo on Diabetes, p. 466.

an imperfect manner, their successive formation in the process of vegetation. The sap is composed of vegetable matter, mixed with several salts which have lime for their basis. Mucilage or gum, which seems to be the first product from it by the powers of the plant, consists of carbon, hydrogen, and oxygen, the general principles of vegetable matter, combined with lime. By a further elaboration the lime seems to be abstracted, and the carbon, oxygen, and hydrogen, alone brought into union: this forms the fecula: and this again, by a change in the proportions of its principles, and particularly by an addition of oxygen, is changed into sugar.

A fact apparently singular was observed by some of the German chemists, particularly by Achard, in their experiments on the production of sugar so as to obtain it economically from different vegetables,—that the exclusion of light from the vegetable, favours greatly its production, so much so, that a plant, the roots or stems of which are sweet while the light is excluded, lose this sweetness when the light is admitted *. But it is known, that the exclusion of light in a growing vegetable, always produces in it an accumulation of oxygen, and, according to the view of the subject now given, will favour the conversion of fecula into sugar. It may be added, that in vegetables the saccharine matter seems to be formed chiefly in the parts secluded from light, as it is most abundant in the roots, and in the sap rising from them, while there is not perhaps an instance of its being discovered in the leaves.

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* Nicholson's Journal, 4to. vol. iii. p. 242. 288.

Sugar is formed however in the fruit of vegetables; and with regard to this Achard likewise mentions a fact which appears at first view contradictory, that the formation of the sugar, contrary to that in the body of the plant, is much promoted by light; this is indeed well enough known with respect to the maturation of fruit. Instead, however, of furnishing any exception to this view of the formation of sugar in the vegetable system, it confirms it; for it is not fecula, but an acid juice, which in the fruit is converted into sugar, and this conversion seems to be effected, as we might *a priori* conclude, by an abstraction of oxygen from the acid.

Mr Cruickshank endeavoured to convert sugar into gum, by the action of substances which might partially abstract its oxygen. He added to a portion of syrup which filled an inverted jar placed over mercury, a little phosphuret of lime; a considerable production of phosphoric gas almost immediately took place; at the end of eight days the syrup was withdrawn; it had no sensible sweet taste, but rather a bitter astringent one; when filtered, alkohol produced a copious white precipitate in flakes, very much resembling mucilage separated from water by the same substance.

" This experiment was somewhat varied as follows: a little refined sugar was dissolved in alkohol, and to this solution a little phosphuret of lime was added; no phosphoric gas was disengaged, nor was there any apparent action produced. More phosphuret being added, the mixture was allowed to remain in an open phial for several days. The alkohol having now evaporated, some distilled water was added; but this produced no disengagement of gas, as the phosphuret had been decomposed, and converted principally into phosphate of lime. The mixture being filtered, and the clear liquor evaporated, there remained a substance extremely tenacious, and which had much the appearance of gum arabic; its taste was bitter, with a very slight degree of sweetness; when squeezed between the teeth it had exactly the feel of gum, but more tenacious. It did not appear to be soluble in alkohol, or at least in any considerable quantity; when thrown upon a red-hot iron it burned like gum, and left a bulky and insipid charcoal.

" It would appear that the saccharine principle had been destroyed in these experiments, and converted into something resembling a gum: that this was effected by the abstraction of oxygen, is rendered highly probable from the nature of the substance employed, and the change which it was found to have undergone; for there are few substances which have so strong a tendency to combine with oxygen, as the phosphuret of lime.

" Some other trials of a similar nature were made, by mixing solutions of sugar with the different sulphurets, and by agitating them with nitrous gas in close vessels. The sulphurets, more especially that of potash, manifestly destroyed the saccharine taste; but on account of the solubility of the different products, the nature of the change could not be so easily and accurately ascertained. The action of the nitrous gas was more doubtful *."

A singular fact with regard to this subject, which I have not found taken notice of by any chemist, was com-

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* Rollo on Diabetes, p. 459.

municated to me by Mr Cameron of Glasgow,—that a solution of sugar may, by particular management, be made to assume the tenacity and thick consistence of strong mucilage. The experiment consists in adding 1½ lb. of syrup (made with 1 part of water to 2 of sugar), to a gallon of water, in a stone bottle, mixing them well by agitation, stopping the bottle closely, and placing it in a temperature of about 50, for three or four days. In this time it assumes a gelatinous consistence, still retaining its saccharine taste, but which in the course of a week or two it gradually loses. By boiling it for some time it loses considerably its gelatinous form, and assumes that of strong mucilage of gum senegal. I have kept it in this state for a considerable time.

It is not improbable, that in this experiment a slight change is produced in the combination of the principles of the saccharine matter, so as to bring it to the state of mucilage: and a curious fact observed by Mr Cameron, that the experiment succeeded only with unrefined sugar, and not either with molasses or with refined sugar, accords with this; unrefined sugar probably containing a small portion of the lime employed in the process of preparing it, and lime being essential to the constitution of mucilage or gum. It has already been remarked too, that a solution of sugar boiled with a little lime, forms a very tenacious liquid.

In the process of fermentation, saccharine matter suffers decomposition, its elements entering into new combinations, whence the formation of ardent spirit or alkohol. The nature of this change is to be afterwards considered.

Sugar is of importance as a substance nutritious and generally agreeable in taste. It exists in the greater part of the vegetable substances that are used as articles of diet, and appears from some facts with regard to its use, to be even in its pure form highly nutritive. Even animals, when partially supplied with it, it has been observed in the West Indies, become fat and vigorous as during the time of the sugar harvest, though they are then kept almost constantly at work. By its antiseptic power it preserves a number of substances from decay or putrefaction, and hence, in confectionary and in pharmacy, is used in the preparation of conserves, syrups, and similar compositions. It is also used in the composition of some varnishes, of ink, and of some pigments, to communicate to them a degree of lustre.

There are some other substances of a saccharine nature, but differing somewhat in their chemical properties from pure sugar, which may be noticed under this section.

Manna is a secreted juice, afforded by several vegetables, but obtained in largest quantity from several species of ash, particularly the Fraxinus ornus, which are cultivated in Sicily and Calabria for its production. It exudes spontaneously from the bark of the tree, but is obtained more copiously by incisions which are made in the stem and branches. When it flows slowly it is more pure: it is collected on straws or chips of wood, and forms what is named Flake manna. When it flows more abundantly it is less pure, and forms the common manna of commerce.

The purest manna is in pieces of a texture somewhat granulated, having a taste that is sweet, but somewhat disagreeable. It is soluble in water and in alkohol. It appears, besides saccharine matter which probably forms its basis, to contain mucilaginous and extractive matter, from which it derives its taste and peculiar qualities. And it is affirmed by Chaptal, that when its solution in water is boiled with lime, clarified with the white of an egg, and concentrated by evaporation, it affords crystals of sugar. He adds, that when decomposed by heat it affords water, acid, oil, and ammonia; its residuum of charcoal also affording alkali.

HONEY is another vegetable product, similar in many of its properties to sugar: it is formed in a number of vegetables in considerable quantity: it is collected by the bee; and many other insects feed upon it. It is always formed in the flower, chiefly at the base of the pistil, and is exposed, frequently by a complicated arrangement, to the atmospheric air: it seems designed to receive and retain the fecundating pollen.

The nature of this product is not very well ascertained. It evidently contains a large quantity of saccharine matter: with this it has been supposed a portion of mucilage is combined, from which it derives its softness and viscosity: And probably its peculiar taste and smell, as well as other qualities which honey from particular plants sometimes has, are owing to a quantity of extractive matter, or of essential oil with which it may be impregnated.' It is entirely soluble in water: by the action of nitric acid it is converted into oxalic acid, one ounce of honey affording, according to Cruickshank's experiments, 4 drachms, 4 grains of acid, a quantity very little less than that afforded by pure sugar.

Lowitz, in the course of his experiments on the effect of charcoal in absorbing the mucilaginous and extractive matter of various substances, supposed that by its agency he might abstract such matter from honey, and obtain its sugar pure. He found, that by adding a sufficient quantity of charcoal to honey, dissolved in water, he deprived it of the smell peculiar to it, and likewise of its taste and colour: but on evaporating the solution, it resumed its colour, and did not shew any disposition to crystallize. On this inspissated liquid, however, being allowed to stand for two months, small masses formed in it of a crystallized appearance: these were obtained pure by diluting the whole with alkohol, which dissolved the glutinous matter, and not the concrete substance: this when dried, formed a powder, which did not attract moisture, and which had a very agreeable sweet taste.

The granulated consistence of white honey, appearing to arise from the concretion of its saccharine part, he endeavoured to separate that part by means of alkohol. He thus procured from 12 ounces of honey, 3 ounces of saccharine matter. This matter still appeared to contain some heterogeneous substance not soluble in alkohol. He therefore boiled pure alkohol on the whole of it: the saccharine part was dissolved, while a quantity of insoluble matter remained on the filtre, through which the liquor had passed while hot. This liquor, after having stood for some days, deposited the saccharine matter in small spherical masses, which accumulating at length, formed a crust quite firm and perfectly white. This matter, however, Lowitz was unable by any process to crystallize, though its texture shewed a kind of crystalline arrangement; exhibiting, when examined by the microscope, a kind of congeries of long needle-like crystals.

This sugar of honey, Lowitz found to differ in the changes it suffers from certain re-agents, from common sugar, particularly from the action of the alkalis and alkaline earths. If lime water be added to its watery solution, which is perfectly limpid, a brown colour is immediately acquired. Quicklime added to the solution while hot, produced a strong effervescence, and the mixture became immediately of a dark brown colour: and by continuing to add lime, the saccharine matter was entirely decomposed: the mixture became black, and emitted a disagreeable smell. The dark-coloured solution contains a large quantity of lime, which is not precipitated by alkalis either pure or in the state of carbonate. If precipitated by sulphuric acid, the residual liquor contains an empyreumatic acid, analogous to malic acid, and convertible into oxalic by the action of nitric acid. If the solution of honey and quicklime is thickened by evaporation, after its brown colour is removed by charcoal, a transparent matter is procured of a light yellow colour, which resembles gum arabic, but has a bitter taste.

The fixed alkalis produce changes on honey, and on the saccharine matter procured from it, the same as those from the action of lime; the honey or the saccharine matter is decomposed with effervescence, and the alkaline taste and qualities, when certain proportions are observed, are lost. Ammonia produces similar effects, but more slowly, and only when its action is promoted by heat [*].

Cavezzali has more lately given a process by which the sugar of honey is obtained in a crystallized state. Its crystallization from common honey he supposed to be prevented by the presence of an acid; and the process therefore which he followed, was, after clarifying white honey, by applying a moderate heat, and removing the scum from its surface, to add to it egg-shells (which consist principally of carbonate of lime) in powder; an effervescence took place; the addition was continued to saturation, and the liquid set aside for some time. A thick scum which formed on its surface was removed, and some flocculi of a mucilaginous matter diffused through it, separated by filtration. A clear syrup was thus procured, free from the sharpness of the honey. At the end of four months, crystals had been deposited from it in a crust at the bottom. This crust was of a red colour, and attracted humidity, but the colour was removed by washing with alkohol, and after this operation it remained dry [†].

More lately Proust has distinguished two species of honey; the one, which constitutes the common yellow honey, of a uniform consistence and viscid; the other, the granulated white honey, which becomes solid, and assumes the form of small spherical masses. He has distinguished also two species of sugar, one soft and not capable of crystallizing, which exists in the grape and other fruits, and in manna; the other, the sugar of the sugar cane. From the white granulated honey he has obtained, by the action of alkohol, a white saccharine powder of an agreeable taste, and which he regards as different from common sugar, and nearly the same with the soft sugar of the grape *. These differences in both cases, however, if they do not arise from intermixture, must depend on very slight modifications of the same species, produced by variable causes, and in part probably by the very operations by which they are recognised, and such distinctions do little more perhaps than load and embarrass the science.

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[*] Journal de Physique, tom. xlii. p. 456.

[†] Annales de Chimie, tom. xxxix. p. 110.

The saccharine matter formed in certain morbid states of the animal economy, giving rise to the disease named Diabetes, appears very similar in some of its properties to the sugar of honey. It suffers nearly the same change from lime: in the experiments made on it by Nicolas, when a little lime was added to its solution, and the whole boiled, on afterwards clarifying it with the white of an egg, the liquor was found to have assumed a reddish brown colour, had lost its sweetness, and become acrid; and when the lime was separated from the combination, by the addition of an acid, the sweetness was not restored †. This is precisely similar to the change the sugar

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* Annales de Chimie, tom. lvii. p. 137, &c.

† Ibid. tom. xliv. p. 65.

of honey suffers from lime, and is different from that which pure sugar undergoes. Cruickshank found, that the saccharine extract formed in diabetes is convertible into oxalic acid by the action of nitric acid *; a property which also belongs to the sugar of honey as well as to pure sugar.

SECT. IV.

GLUTEN.

ALONG with the fecula and saccharine matter which compose the principal part of the nutritive grains, there exists another substance, approaching more nearly in its characters to animal matter than any other product of the vegetable system. From the resemblance in its properties to the animal principle formerly named Gluten, it has received the name of Vegetable Gluten. It has been believed likewise to exist in the juices of plants, and in some of their secreted products; but it is more easily separated from the farina of the nutritive grains, and it is from the gluten obtained in this manner that its characters are derived. Its existence was distinctly pointed out, more than seventy years ago, by Beccaria, to whom we are indebted for the simple analysis of the nutritive grains by which it is obtained.

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* Rollo on Diabetes, p. 429.

In the process of obtaining the fecula of wheat, the flour is made into a paste with water, and kneaded in the hand, or rather in a coarse linen bag, water being poured on it, until the fecula is carried off suspended in the water, and the sugar and other soluble principles in a state of solution. There remains, at the end of this process, a soft viscous substance, of a fibrous texture, possessing great tenacity and elasticity. It is this which is denominated Gluten. It is obtained in largest quantity from wheat; the quantity, on an average, amounting to about a twelfth part of the weight of the flour of that grain; or taking into account the weight of the water with which it combines in its extraction, it varies, according to Beccaria, from a third to a fifth of the weight of the flour. It is contained in much smaller quantity in the other nutritive grains, and can, indeed, be scarcely extracted from any of them. Beccaria, however, found traces of it in maize; and Fourcroy and Vauquelin, in their experiments on the different nutritive grains, have found, that a principle possessing the characters of animal matter, and therefore probably gluten, exists in barley, garden beans, and lupines. It cannot be discovered in rice; nor are there any traces of it in the potatoe, or other nutritive roots.

Gluten has also been supposed to be contained in the expressed juices of a number of plants. Rouelle had observed, that, in subjecting to pressure the fresh leaves of a number of vegetables, it deposited, on standing, a matter which, from its colour, he named Green Fecula; and in this substance he discovered the existence of a principle which he considered as analogous to the gluten of wheat. Fourcroy supposed this principle to be different from gluten, and to approach in its nature to the animal principle denominated Albumen, whence he named it Vegetable Albumen. We shall find reason, however, to conclude, that the original opinion of Rouelle is probably more just, and that this principle may rather be regarded as a variety of gluten.

The gluten obtained in the analysis of wheat flour, above described, is a solid but soft viscous substance, extremely tenacious, so that it can be drawn out to a great length, and moulded into any form: it is also highly elastic, so that when drawn to a great extent, it quickly resumes, when left to itself, its former volume: its texture is distinctly fibrous, or it appears to be composed of threads. It has scarcely any taste, and a faint odour: its colour is greyish, and, when dried, it is semi-transparent, having then some resemblance to glue in its appearance. In its soft state it is extremely adhesive to the touch, and has, from this property, even been used as the basis of cement, for uniting fragments of porcelain or glass.

When exposed to the atmosphere, gluten remains for some time soft, acquiring a darker colour. If exposed to a dry and rather warm atmosphere, it dries slowly, loses its ductility and elasticity, and suffers no farther change. This induration of it is still more complete, when a moderate heat is slowly applied to it; it may then be rendered hard and brittle. But in a humid atmosphere, soft gluten retains its softness, and soon passes into a state of putrefaction, swelling up, and acquiring an offensive odour,—changes which are accompanied with a formation of ammonia, acetic acid, and an oily matter [*]. If it has not been entirely deprived of the fecula of the wheat, this, according to Macquer's observations, suffers the acetous fermentation; and the re-action of this small portion of acid, with the slow action of the air and water, converts the gluten into a substance, which, as Rouelle remarked, has a very near resemblance to cheese, and which, by the addition of salt, may be preserved in that state [†]. It then contains ammonia and acetic acid.

When kept immersed under water, it does not immediately putrefy; a formation of acetous acid takes place, and, at the same time, ammonia is formed, which combines with this acid, though not in quantity sufficient to saturate it. This evolution of acetic acid appears, as Vauquelin has remarked, to check the progress of the putrefaction; and, by its action, a portion even of the remaining gluten is dissolved by the water [‡]. In this state of solution, it gradually putrefies, separating in mucous pellicles.

The portion of gluten that remains undissolved, after this kind of fermentation which it has suffered, if immersed anew in water, begins again to ferment, disengages carbonic acid, becomes of a purple colour, and emits a fœtid odour, similar to that from putrid animal membrane. After three months of this slow putrefaction, it has acquired a brown colour, exhales only a faint smell, is much diminished in volume and quantity: when dried, it formed small masses, which softened under the finger like wax, melted and burnt with flame, and was soluble in alkohol, which it coloured brown; a portion which remained undissolved being in the state of a powder, inodorous, insipid, and very similar to charcoal powder, but burning with an acrid odour, and affording ashes, in which iron and silex were discovered. In this series of changes, a portion of the nitrogen and hydrogen of the gluten have united to form ammonia; part of its carbon has formed, with oxygen, carbonic acid; another portion of carbon, with hydrogen, has formed the unctuous matter; and the remaining elements have formed the residuum [*].

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[*] Annales de Chimie, tom. xxxviii. p. 259.

[†] Fourcroy's System, vol. vii. p. 417.

[‡] Annales de Chimie, tom. xxxviii. p. 259.

It is doubtful if gluten is soluble in pure water. When water is allowed to remain over it for some time, its transparency is impaired, and a mucous matter appears to be dissolved, or rather suspended in it: by filtration, it may be rendered limpid: when heated, a glutinous matter separates in flocculi; and a precipitate is thrown down by oxymuriatic acid, and by tanin. Hence Fourcroy has concluded, that gluten is soluble in water [†]. But it is not clear, that these phenomena depend on the presence of pure gluten in a state of solution; and it is probable, they are connected with the changes in composition which the gluten itself has suffered, and probably with the production of acetous acid, from its partial decomposition. When water is boiled on gluten, it contracts, becomes more solid, and loses its tenacity and ductility.

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[*] Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

[†] Ibid. p. 3.

Gluten is likewise insoluble in alkohol: alkohol even precipitates the small portion of it which exists in water in a state of solution, when the water has been macerated on it. If gluten, however, which has been kept for some time under water, so as to have passed into the acid fermentation, be triturated with a portion of alkohol, it is partially dissolved, and a liquid of a thick consistence formed. If more alkohol be added to this, part of the gluten is precipitated, but a portion still remains in solution, and by filtration a transparent liquid is obtained. This is decomposed by water, gluten being precipitated. By evaporation of the spirituous solution, the gluten is obtained dry, brittle, and shining. Cadet, by whom these experiments were made, has remarked, that the thick solution of fermented gluten in alkohol forms an excellent varnish, as it is transparent, adheres strongly, has a degree of elasticity, and does not scale off. A similar varnish is obtained by dissolving the gluten in acetous acid; but that formed by alkohol is preferable. This latter solution also forms a cement for porcelain, and an excellent basis of paints *.

Gluten is dissolved by alkaline solutions, when their action is promoted by a moderate heat. On the addition of an acid to the solution, the glutinous matter is precipitated, but so far changed as to be no longer elastic. In a concentrated state, they still more evidently decompose it, form a kind of soap, while there is at the same time a production of ammonia.

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* Philosophical Magazine, vol. xiii. p. 9.

The changes produced in gluten by the acids are different according to the nature of the acid, and its concentration or dilution. Some of the weaker acids, as the acetic, dissolve it, though not without some change, as, during the solution, a portion of ammonia is generally formed; and when the acid is neutralized by an alkali, the gluten is precipitated with the loss of its ductility: Fourcroy has affirmed, however, that it is precipitated with its properties unaltered *. When it has undergone the slight fermentation which it suffers when kept under water, it is still more soluble in acetic acid; and a portion of it appears from Vauquelin's experiments, to exist dissolved in the sour liquor obtained in the preparation of starch from wheat, probably by the medium of the acetous acid, and in consequence of this slight change †. Hence, as he has observed, the necessity, in the preparation of starch from wheat, to allow the liquor above the fecula to run into the acetous fermentation, and in its acid state to remain over it for some time; the acetous acid dissolving the portion of gluten which still adheres to it, and thus rendering the starch more pure, of a whiter and more brilliant colour, and more loose and dry; while in the preparation of starch from the potatoe, or from other roots or grains which do not contain gluten, this is not requisite.

Sulphuric acid in its concentrated state blackens gluten, and causes a formation of acetic acid and of ammonia, with an evolution of carburetted hydrogen. Nitric acid

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* Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

† Annales de Chimie, tom. xxxviii. p. 259, 261.

disengages from it nitrogen gas, and gives rise to the production of a portion of oxalic and malic acids. Muriatic acid acts on it very slowly, and in a manner somewhat similar to the acetic. Oxymuriatic acid softens gluten, and changes it into a yellowish flocculent matter. It also precipitates it from any combinations in which it is in a state of solution, and thus affords a test by which its presence may be recognised.

This, like the other immediate principles of vegetables, is decomposed by heat; but the products from its decomposition are peculiar, and are the same as those of animal matter. When exposed to a moderate heat, it swells considerably. If placed on burning fuel, it becomes quite soft or semi-fluid, and burns with a fœtid odour. If subjected to destructive distillation in a retort, it affords carbonate of ammonia partly concrete, partly in solution in water, a large quantity of a thick empyreumatic oil, and a little prussic acid: there is disengaged also carburetted hydrogen gas; and the remaining charcoal, which is in considerable quantity, is of difficult incineration. From the production of ammonia, it is obvious that nitrogen enters into the composition of gluten: from the large portion of oil which it likewise affords, it must contain much hydrogen, while none of the products indicate the presence of oxygen in any considerable proportion. Phosphorus also appears to exist in its composition. Vauquelin found, that the liquor formed in the preparation of starch from wheat, contained a portion of phosphoric acid in combination with lime, probably derived from the gluten of the wheat; and the phosphate of lime found by the same chemist to exist in the ashes of wheat-flour, has probably the same origin. In its analysis, therefore, gluten presents all the characters of animal matter, as it does also in being liable to putrefaction, and in affording nitrogen from the action of nitric acid.

Gluten appears to have the property of promoting fermentation; and the action of yeast in exciting this process, has been supposed to depend on the gluten it contains. Vauquelin has remarked, that the water in which gluten has been macerated for some time, converts sugar into excellent vinegar without effervescence, and without the contact of the air *.

From the nature of this principle, it must contribute much to the nutritious quality of the grains in which it exists, as containing all the principles which are required for animal nutrition: hence the superiority of wheat, which contains it in so large a proportion, to the other nutritive grains. It is on the presence of this principle too, that the superior quality of bread from wheat, compared with that from the other grains or roots depends, as Beccaria remarked. The flour of these forms with water a solid friable paste; while the flour of wheat forms a paste that is ductile and elastic, in consequence of the developement of its glutinous part, this gluten forming the body of the paste through which the fecula and saccharine matter are diffused; and when the slight fermentation which it suffers, probably from changes in the saccharine matter, favoured by the presence of the gluten, takes place, this paste is rendered spongy and porous, from the disengagement of the carbonic acid gas from the

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* Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

fermentative process, while it still retains in some measure its elasticity; and hence the lightness and porosity of well-baked wheaten bread. Bread possessing these qualities, cannot be prepared from the farina of oats, barley, rye, or rice, or from that of any of the nutritive roots, as in all these the quantity of gluten is very inconsiderable, and in some of them no trace of it can be discovered.

It has been long known, that the expressed juices of a number of plants, as scurvy grass, cresses, and others of the cruciform kind, contain a principle which is analogous in its properties to animal matter, which like it is liable to putrefaction, and evolves ammonia during its decomposition. Rouelle, I have already remarked, regarded this principle as a variety of vegetable gluten, and he supposed it to form the basis of the green fecula which is contained in the expressed juices of a number of plants. Fourcroy, a number of years afterwards, finding that this principle exists in solution in these juices; that it is separated by coagulation by heat; that it is also coagulated by acids, while it is dissolved by alkalis,—properties in which it approaches to the proximate principle of animal matter, denominated Albumen,—considered it as different from gluten, and gave it the name of Vegetable Albumen[*]. Proust has more lately called in question the opinion of Fourcroy, and revived that of Rouelle: and the question as to the nature of this principle, is involved in some uncertainty. It wants some of the physical characters of gluten, but this may be owing to the form in which it is obtained; it approaches to it in several of its chemical characters: on the other hand, it has unquestionably some points of resemblance with animal albumen, and there is, therefore, a difficulty in deciding whether it can be regarded as perfectly identical with the gluten of heat. It is so nearly so, however, that its history may be considered under this section.

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[*] Annales de Chimie, tom. iii. p. 252.

If scurvy grass, cabbage, cresses, or horse-radish, in their recent state, be subjected to pressure, the juice that is obtained is somewhat turbid; but, on raising its temperature to between 170° and 212°, small flocculi are formed, which are diffused through the liquid, or subside from it, and are easily separated by filtration. It is this matter which Fourcroy considers as vegetable albumen, or which, with Rouelle and Proust, we may regard as analogous to gluten.

In its separation, part of the green colouring matter of the plant, in a state somewhat similar to fecula, and sometimes of a resinous nature, adheres to it; but Fourcroy succeeded in separating this, by the following process: The juice of young cresses being passed through a paper filtre, left the grosser fecula suspended in it on the filtre: the filtered liquid, though limpid, was of a green colour; but after exposure to the air for two hours, it became turbid, and, on being filtered again, became limpid, leaving a quantity of green fecula on the filtre. On now plunging the vessel containing it into a bath of boiling water, in a few minutes it became turbid, and a whitish coagulated matter separated from it. Another portion of the juice, left exposed to the air for two days, deposited similar flocculi; and they were also separated by the addition of sulphuric acid *.

This concrete matter was found by Fourcroy to be insoluble in water, even when boiling: it gave a green tinge to paper coloured with mallow flowers: the alkalis dissolved it readily: macerated in water, it swelled, became soft, exhaled a fœtid ammoniacal odour, and passed to a state of putrefaction: exposed to a dry and warm atmosphere, after having been pressed between bibulous paper, it acquired a degree of ductility and transparency similar to that of glue: subjected to destructive distillation, it afforded a large portion of ammonia.

These characters are equivocal, if regarded as serving to determine that this is a principle distinct from gluten, and analogous to animal albumen.

The most characteristic property of this last substance is its being coagulated by heat, separating from the liquid in which it is dissolved, and assuming a flocculent form. So far this principle contained in these vegetable juices resembles albumen. But in the history of gluten it has appeared, that, by the medium of certain re-agents, of a very small quantity, for example, of acetous acid, it may exist in solution in water; and that, when this liquor is heated, the gluten separates in flakes. Proust has remarked, too, that the coagulation of this matter from the vegetable juices takes place at 145° of Fahrenheit, while albumen does not at that temperature experience the

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* Annales de Chimie, tom. iii. p. 257.

slightest change. He has farther found, that when the vegetable juice is largely diluted with water, as with 20 parts, the peculiar matter still separates from it by coagulation, when the temperature is raised; while animal albumen, equally diluted, does not coagulate when heated, the liquid becoming opalescent; and no flocculi separate, even when the liquor is boiled [*].

This vegetable principle is coagulated by acids,—a property in which it resembles albumen. But the gluten of vegetables is also precipitated by some of the acids. Alkohol throws down the vegetable albumen, as it has been named, in the state of an opaque whitish powder; while it precipitates animal albumen in light flocculi.

This principle is dissolved by alkalis. But the gluten of vegetables is also dissolved by the alkalis: this latter principle does not, indeed, appear to be so easily soluble as the other; but this difference may arise from the state of aggregation, or from some very slight modification of composition.

The other characters enumerated by Fourcroy, as serving to connect this substance with albumen, are less appropriate. Insolubility in water, being liable to putrefaction, and evolving ammonia, either when suffering this change, or when decomposed by heat, are all characters belonging to vegetable gluten, as well as to animal albumen.

One property assigned to it by this chemist, which is peculiar to albumen, is changing some of the vegetable colours, as that of mallows, to a green. But according to

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[*] Philosophical Magazine, vol. xvii. p. 23.

Proust, when it is washed it does not produce this change, and the juices in which it is contained have no such property; some of them even, as the juice of cabbage or hemlock, render litmus red. When the vegetable principle does possess this property, therefore, it is probably owing to the evolution of ammonia.

Proust has pointed out other properties in which this principle differs from albumen, such as that of being precipitated by a number of neutral salts, which do not render albumen turbid; and being much more liable to spontaneous decomposition than albumen. The question, however, is not so much, whether this principle is perfectly the same with albumen, as whether it is essentially different from the gluten of wheat; and the preceding facts appear to prove, that the differences between them are not considerable, and not sufficient to characterize them as distinct principles.

One circumstance which confirms this, and strengthens the suspicion, that this matter, separable by coagulation from a number of the vegetable juices, is merely vegetable gluten somewhat disguised by the state in which it exists, is, that it exists in the water employed in preparing the fecula or starch from wheat-flour, and is separated from it by coagulation by heat, as Fourcroy has remarked, in the same manner as from the expressed juices. It is rather more probable, that a portion of the gluten known to exist in this flour shall be in solution, and be the substance separated in this manner, than that it shall be a distinct principle, especially as it is proved, that the solubility of gluten is promoted by the action of acetic acid, and that this acid is contained in the water employed in the preparation of starch. Proust has accordingly observed, that this matter suffers changes like gluten: kept in a humid state, it forms acetic acid and ammonia, and like gluten, acquires the odour and taste of cheese; and Fourcroy has even observed, in his late researches with Vauquelin on the analysis of the farina of wheat, that it is analogous to gluten *.

It is to be observed, too, that there must be considerable difficulty in obtaining this principle, so as to have all the physical qualities of gluten by any other process than that by which we obtain the gluten of wheat. Fourcroy himself has justly observed, that if a different process be followed with regard to this very substance,—if, instead of being made into a paste and kneaded with water, it be diluted at once in a large quantity of water, the separation of the fecula no longer properly takes place, and the gluten is no longer obtained. It then probably exists in the water in precisely the same state as in the vegetable juices, and may perhaps be capable of being separated by a process similar to that which is applied to them.

According to Proust, the principle now described exists in a great number of plants. It is found in the expressed juice of borage, elder, and buckthorn; also, in grapes, quinces, apples, and other fruits; and in the acorn, chesnut, horse-chesnut, rice, barley, rye, pease, and beans of all kinds †.

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* Annales du Museum d'Histoire Naturelle, tom. vii. p. 3.

† Philosophical Magazine, vol. xvii. p. 31.

SECT. V.

ALBUMEN.

THOUGH the principle which has hitherto received the name of Vegetable Albumen appears to be merely a variety of gluten, there is reason to admit the existence of a vegetable product, to which that name may be with propriety applied, as, in the greater number of its properties, it has a strict resemblance to animal albumen. It exists in the juice of a plant, a native of the Isle of France, the Carica papaya, and has been made the subject of experiment by Vauquelin *, and by Cadet †. Of all the products of the vegetable system, it is the one which approaches most nearly to animal matter; and it might indeed be regarded as a variety of it, if its origin were not known.

The juice which contains this principle issues from the tree white as milk: in a few minutes it coagulates; flocculi of a white matter like cheese separate, and swim in the liquid part, which, after the coagulation, is transparent. The juice is diffused through all the parts of the tree, but is most abundant in the fruit while unripe.

The experiments of Vauquelin were made upon this substance in three states: 1st, In the solid state to which it had been reduced by exposure to the sun; 2dly, In its

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* Annales de Chimie, tom. xliii. p. 267.; tom. xlix. p. 295.

† Ibid. tom. xlix. p. 250.

natural state, it having been preserved in bottles well closed; and, 3dly, In the state of the natural juice, mixed with sugar to preserve it without alteration.

The juice inspissated by exposure to the sun, is of a yellowish white colour; some parts of it are even of a pure white and semi-transparent. It is brittle and easily reduced to powder when it is very dry: it melts easily in the mouth, impressing a singular taste, and exciting a copious discharge of saliva. It attracts humidity from the air, and changes into a viscid paste. It is dissolved readily by cold water, and still more quickly and abundantly by warm water; a small quantity of a white matter only being left undissolved, which has an unctuous appearance, which melts easily, and diffuses an odour similar to that of empyreumatic fat. Its concentrated solution becomes turbid and coagulates on ebullition; but the whole of the dissolved matter does not separate, as a portion is afterwards precipitated by other re-agents. Alkohol added in large quantity to the watery solution of the juice, precipitates it completely, and without occasioning in it any alteration. Sulphuric, nitric, and muriatic acids, coagulate it abundantly; and a precipitation is even occasioned by a number of metallic solutions, as those of quicksilver, silver, and lead. Exposed on burning fuel, it burns, decrepitating slightly, and diffusing a very fœtid ammoniacal odour, as animal substances do. Subjected to destructive distillation, it gives much carbonate of ammonia; a thick black oil, the greater part of which falls to the bottom of a brown liquid, which is produced at the same time; carbonic acid, and carburetted hydrogen gases are disengaged, and there remains a charcoal light, difficult to burn, and which leaves as ashes, a little earthy matter consisting of lime, and phosphate of lime. Distilled with weak nitric acid, it gives a large quantity of aërial fluid, consisting of carbonic acid, and nitrogen : and in dissolving in the acid, it communicates to it a yellow colour and a very bitter taste. There is also formed a large quantity of prussic acid, and oxalic acid. Lastly, it is liable to putrefaction : its watery solution decomposes when kept, and acquires a fœtid odour, as animal matter does.

With regard to the liquid juice, on opening the bottle in which it was preserved, an elastic fluid was disengaged with such violence, as to throw part of the liquid to a distance : this gas was ascertained, both by Cadet and Vauquelin, to be carbonic acid, produced no doubt by the decomposition of some principle contained in the juice. Masses of a white matter similar to cheese, floated in the liquor : these in drying, assumed the semi-transparence of horn : the dried matter softened when heated, and exhaled a white vapour, with an odour similar to burnt unctuous matter : it dissolved abundantly in warm alkohol, from which it in part separated again in cooling. This matter, evidently sebaceous, appeared to Vauquelin to have originated in the decomposition of the juice itself.

The liquid part contained a principle which had properties similar to those of the inspissated juice, with a portion of acetic, not malic acid as Cadet had announced, originating probably from decomposition, as there is no sensible acidity in the inspissated juice. Its odour was fœtid and very disagreeable : it had a taste at once acid, bitter, and astringent. When rendered limpid by filtration, it had still the same taste and smell. The acids coagulated it into a mass very thick, which had a great resemblance to the white of an egg, or to dried albumen. The action of oxymuriatic acid was rather peculiar: when added in small quantity, it gave a rose colour; in a larger quantity a violet; and in a still larger quantity, it entirely destroyed the colour: and as these phenomena did not appear when this acid was added to the inspissated juice, it follows, that some change must have taken place during the inspissation, subversive of the property of forming these colours. Pure potassa formed, when added to the filtered liquid juice, a precipitate of a white colour, and at the same time caused the exhalation of a strong ammoniacal odour. The liquid when filtered after this, still assumed a violet colour, from the addition of oxymuriatic acid. Alkohol added to the juice evaporated until it had acquired the consistence of a syrup, produced a very abundant precipitate. The infusion of galls formed also a precipitate in large quantity.

The juice that had been preserved with the addition of sugar, had not suffered any particular change; for when the sugar was separated by alkohol, it presented the same properties as the concrete natural juice.

Vauquelin also examined a quantity which had been preserved by mixture with rum, but it appears to have undergone a greater change in its properties.

Vauquelin observes, that from these experiments there can be no doubt, that the juice of this tree is composed principally of a matter which has all the characters of animal substances. It is not perfectly the same with any known vegetable principle, but it approaches most, he adds, to albumen; since, when dry, it dissolves like it in water: the solution too, like that of albumen, is coagulated by heat, by acids, alkalis, metallic solutions, infusion of galls, and alkohol; *and, lastly, it affords by decomposition* by heat, or by the action of nitric acid, absolutely the same products that animal substances the most completely characterized do. It may, therefore, properly receive the name of Vegetable Albumen. We cannot, continues Vauquelin, regard without interest a substance produced by a vegetable, presenting all the characters of animal matter; and we perceive from this example, that nature has given to certain species of plants, the power of forming combinations similar to those produced in the animal machine,—a fact indeed established, though undoubtedly in a less striking manner, by the production of gluten in the vegetable system.

SECT. VI.

GELATIN OR JELLY.

THE juice of certain fruits, as the currant, when expressed, if not too watery, concrete into a kind of tremulous jelly. There is none of the known principles of vegetables to which this property can well be assigned: it is one, too, extremely characteristic, and until the subject be farther investigated, it is necessary to consider it as distinctive of a peculiar principle, to which the name of Gelatin or Jelly may be given. There is an animal principle which has received the name of gelatin, which has likewise the property of forming, with a certain proportion of water, a tremulous jelly, but, except in this particular, *vegetable jelly appears to have no similarity to it nor does it even appear to approach to animal matter* in its chemical characters or composition: it is not liable to putrefaction, but suffers that slow decomposition which vegetable matter in a humid state usually undergoes.

Scarcely any observations have been made on this principle, except what has been incidentally stated by Vauquelin in the course of his analyses of different vegetable substances, particularly in a memoir on the analysis of the fruit of the Tamarind [*], and in another on the analysis of the pulp of the Cassia fistula [†], in both of which it is contained.

It is soluble only in small quantity in cold water, even with agitation, but boiling water dissolves it abundantly, and the solution forms a jelly when it cools. It is necessary, however, to obtain the gelatinous consistence, that there should be a certain proportion between the gelatinous matter and the water; and if boiled a long time with water, it loses the property of forming a jelly. Hence the reason, as Vauquelin has remarked, that in the preparation of the vegetable jellies which are formed by boiling slightly the juices of certain fruits with sugar, it often happens, that if the proportion of sugar is not sufficiently large to absorb the water of the juice, or form with it a syrup, and if, in consequence, it is necessary to boil the liquor to dissipate part of the water, it does not concrete into a jelly on cooling, and the property may even be entirely destroyed.

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[*] Annales de Chimie, tom. v. p. 101.

[†] Ibid. tom. vi. p. 282.

Jelly may be obtained in a solid form by drying. That from the pulp of the tamarind, Vauquelin found to be transparent.

This principle, at least that variety of it obtained from the pulp of cassia, unites easily with alkalis: nitric acid, in affording to it oxygen, causes it to pass into oxalic acid, without disengaging from it any sensible proportion of nitrogen. When subjected to destructive distillation along with the elastic fluids usually obtained from the decomposition of vegetable substances, it affords much pyromucous, or empyreumatic acetic acid, very little oil, and almost no ammonia. When burnt, its ashes, which are in very small proportion, contain a little carbonate of potassa, carbonate of lime, argil, and oxide of iron.

Fourcroy has supposed that this gelatinous matter is a combination of mucilage and vegetable acid;—an opinion that is vague, and liable to the objection that we do not perceive how the addition of the acid could so far modify the properties of mucilage, nor have we any proof that it could produce such an effect.

SEGUIN had supposed, that a principle still more strictly analogous to animal gelatin exists in some vegetables, particularly in Peruvian bark, its presence being recognised, as he supposed, by a character peculiar to animal gelatin, that of forming an insoluble magma or precipitate with infusion of tanin. In this principle he even supposed that the febrifuge power of this bark resided, and, with much confidence recommended animal glue as a substitute [*]. On this subject some experiments were made by Dr Duncan *junior*. He found, that a principle does exist in Peruvian bark, which combines with tanin, and forms a compound sparingly soluble in water. But this principle is in no other property analogous to gelatin. Its solution has no tendency to assume a gelatinous consistence; and it is not precipitated as animal gelatin is, by carbonate of potassa. It is also soluble in alkohol, while gelatin is precipitated by alkohol from its watery solution. And it does not even separate from a watery solution of tanin, all that is precipitable by a solution of gelatin. Until the characters of this principle are more fully determined, Dr Duncan has proposed to distinguish it by the name of Cinchonin [†].

SECT. VII.

CAOUTCHOUC.

CAOUTCHOUC, or, as it is usually though improperly named, Elastic Gum, is a vegetable matter, which in several of its physical qualities, as well as in its chemical relations, has some similarity to vegetable gluten, and which so far agrees both with it and albumen, as to approach in the nature of its composition to animal matter,

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[*] Nicholson's Journal, vol. vi. p. 136.

[†] Ibid. p. 225.

It in some measure connects also the preceding principles with those which are to follow, and I therefore place it in this part of the arrangement.

The substance to which the name of Caoutchouc or Elastic Gum has been more particularly given, was brought from Spanish America, in the form of hollow spheres or bottles, in which state it is still imported into Europe; it was evident, therefore, that it had undergone some artificial preparation. Condamine gave the information, that it is the inspissated juice of a tree belonging to the family of the Euphorbia, which has since received the botanical name of Hævea guianensis, or Hævea caoutchouc. Incisions are made in the bark of this tree: a milky juice exudes, which is collected. It is applied, in successive coatings, over a mold of clay; is dried by exposure to the sun, and afterterwards, by being placed in the smoke from burning fuel; when dry, the clay mold is crushed, and the fragments extracted, and in this manner the spherical bottles are formed.

It has since been discovered, that caoutchouc is not exclusively the produce of this vegetable, but that it is furnished likewise by other plants, either perfectly the same, or with very slight variations of properties. It is obtained in large quantity from the Jatropha elastica, a native likewise of different provinces of South America. Dr Roxburgh has described another vegetable, a native of India, the Urceola elastica, which affords a juice, which when thickened has all the properties of the American caoutchouc; and he has farther observed, that there are many other trees, natives of the torrid zone, that yield a milky juice, possessing qualities nearly of the same nature; as Artocarpus integrifolia, Ficus Indica, Ficus religiosus, Hippomane biglandulosa, Cecropia peltata, &c *.

Fourcroy procured specimens of the juice of the caoutchouc in the state in which it exists previous to its inspissation, from the island of Bourbon, from Cayenne, and the Brazils, and examined its properties. Each of these contained a white turbid liquor, of an unsupportable fœtid smell; in the midst of which was a white concrete matter, rather spongy at its surface, very elastic, of a soft, fine, and close texture. 'These concretions had the form of the bottles that contained them, but were less in size: they had been deposited by time, and without evaporation, for the bottles were well closed, and had lost nothing. The juice, when exposed to the air, became very speedily covered with a crust of elastic gum. In a vessel filled with oxygen gas, the liquid afforded an elastic pellicle more speedily, and a very sensible absorption of gas took place. Alkohol separated flakes, and oxymuriatic acid immediately formed an elastic precipitate. From these experiments he concluded, that caoutchouc exists ready formed in the juice of the tree, and is capable of being separated in the concrete form; but that a portion also exists not sufficiently perfect to be deposited with its elastic property; that it acquires this, together with its inspissation, from the action of oxygen; and that by this operation, exposure to the atmosphere influences the concretion of caoutchouc in the usual process in which it is brought to the solid form †. Dr Roxburgh has likewise observed, that

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* Nicholson's Journal, 4to, vol. iii. p. 435.

† Annales de Chimie, tom. xi. p. 228.
Chemical System, vol. viii. p. 46.

the milky fluid which oozes from incisions in the bark of the Urceola elastica, separates on exposure to the air into a firm elastic coagulum, and a watery liquid; the coagulum becoming of a darker colour from the action of the air, and being no longer soluble in the liquid, though before intimately blended with it. The purest caoutchouc Fourcroy supposes to be that which separates spontaneously from the juice in close vessels. It is white, or of a slight fawn colour.

The properties of caoutchouc have been determined, however, principally from the state in which it exists in the elastic bottles which are imported to Europe; and in this state its properties do not seem to have undergone any important change, or to be different from those of the pure caoutchouc. Its colour is a light brown; its external surface is smooth; its internal texture is rough, and presents a fibrous appearance. Its specific gravity is nearly the same with water, being from 9.3335, to 10.000. It is inodorous, and is also destitute of taste.

The most remarkable physical property of which this substance is possessed, and which eminently distinguishes it, is its high elasticity. It can be stretched out to a great length, and when the force that has been applied to it is withdrawn, it instantly returns to its former dimensions. Its pliancy is increased by heat, while it is rendered more rigid by cold; and its softness, which is connected with the former quality, is so much increased by warmth, that it can be moulded into any form, and two parts newly cut may even be pressed together, so as to be intimately united. A circumstance rather singular has been observed by Mr Gough, with regard to its extension, that when it has been rendered quite pliant by heat, as by keeping it for a short time in water at 130°, on stretching it suddenly, its temperature is raised, as may be perceived by making the experiment upon it, kept in contact with the lips, and on permitting it suddenly to contract, the temperature falls; the density being probably augmented by the stretching, and being accompanied therefore with a diminution of capacity. Accordingly Mr Gough found, that the specific gravity of a slip of caoutchouc is increased by keeping it extended, while it is weighed in water. He has also remarked, that if caoutchouc be stretched, it does not easily recover its dimensions, if the temperature be diminished, but its elasticity is immediately restored by moderate warmth *.

Caoutchouc, exposed in a dry state to a high temperature, softens, swells up, and emits a fœtid odour similar to that of animal substances: as the heat is increased, it melts into a viscid matter, and remains in this state when cold. If heated sufficiently high, it takes fire, and burns with a vivid light, and dense smoke: in the countries in which it is produced, it has been used for torches.

This substance is perfectly insoluble in water: it is softened when immersed in warm water, as has been already remarked, an effect depending rather on the temperature, than on the agency of the water. Even when the water is boiled on it for a long time, it preserves all its softness and elasticity, and suffers no apparent change.

It is also insoluble in alkohol: by boiling the alkohol upon it, it is deprived only of the carbonaceous matter

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* Manchester Memoirs, New Series, vol. i. p. 288.

which is interposed between each layer of it, as usually prepared: it is therefore by this operation rendered colourless, and the layers become more apparent.

Ether, a product of alkohol, dissolves it. Macquer observed, that highly rectified sulphuric ether dissolves it readily; and by evaporation, the caoutchouc may again be obtained in the solid state unchanged. Berniard, on the contrary, found caoutchouc insoluble in sulphuric ether, —a difference of result, explained by a fact discovered by Cavallo, that ether is a proper solvent of this substance, only when it has been previously well agitated with water; by which the small portion of sulphurous acid it contains at its first production is removed. Pelletier discovered, that if the caoutchouc be previously boiled in water, until it is swelled and softened, it is easily and completely dissolved by the ether, and a very saturated solution obtained *. Berniard discovered, in the series of experiments which he published with regard to this substance †, that it is dissolved speedily in nitric ether, the liquid acquiring a fine yellow colour, even in the cold; and when heat was applied, the whole nearly of the caoutchouc was dissolved. At the same time he observed, that this can scarcely be considered as a proper solution, but that it is rather owing to the decomposition of the caoutchouc, by the action of the nitric acid contained in the nitric ether: and he accordingly found, that when the solution was evaporated slowly, a substance was obtained of a rich yellow colour, transparent, friable, and

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* Memoires de l'Institut. National, tom. i. p. 56.

† Journal de Physique, tom. xvii. p. 277.

entirely soluble in alkohol, having therefore all the characters of a resin, and which was not elastic. Dr Roxburgh did not find the caoutchouc of the *urceola* soluble in nitric ether, perhaps from the ether he used having been free or nearly so from nitric acid.

Macquer found, that the volatile oils dissolve caoutchouc by the assistance of heat: this was confirmed by Berniard, who examined several of these solutions, as those formed by the oils of lavender, spike, and turpentine. These solutions are viscid, and even when inspissated remain clammy. He found, that it was likewise dissolved readily by the fixed oils when they were boiled on it, and also, though more sparingly, by melted wax.

The alkalis, according to Berniard's experiments, do not dissolve caoutchouc in the cold: when macerated for six days in soapmakers' ley, it was not sensibly altered; but on boiling them for half an hour, it was corroded.

The acids act upon it, not merely as solvents, but decomposing it. In Berniard's experiment, sulphuric acid did not act immediately on pieces of caoutchouc immersed in it, but at the end of fifteen days the acid was coloured: it at length became perfectly black, and each remaining fragment had the appearance of a piece of charcoal. The acid when distilled, passed over almost entirely in the state of sulphurous acid. Weak nitrous acid, digested in the cold on a piece of caoutchouc, produced in six days no sensible change, but at length gradually corroded and hardened it, rendering it yellow: the strong fuming acid decomposed it very quickly. Muriatic acid, either in the cold or with the assistance of heat, did not sensibly alter it: and even at the end of two months, the caoutchouc immersed in it had preserved its colour, elasticity, and weight. Acetic acid, in the state of distilled vinegar, had no effect whatever upon it *.

Caoutchouc, decomposed by heat in close vessels, afforded, in an experiment made by Berniard, a watery liquid, and an empyreumatic oil, with ammonia: the elastic products he did not collect: there remained a quantity of charcoal. In this analysis, imperfect as it is, we perceive the approximation of this substance in composition to vegetable gluten. Fourcroy found too, that caoutchouc treated by nitric acid afforded nitrogen gas, with carbonic, prussic, and oxalic acids †.

This substance is capable of being applied to important purposes, from its softness and flexibility, its elasticity, and particularly its indestructibility, and not being affected by air, water, or indeed the greater number of chemical agents. Tubes for conveying gases, and other chemical instruments, are accordingly prepared from it: and bougies, catheters, and similar surgical instruments of caoutchouc, are much preferable to what can be prepared from any other substance. The difficulty, however, in applying it to these uses, and which renders instruments prepared from it of a high price, is that of finding a solvent which can dissolve it without alteration, so that by inspissation, it can be obtained with its elasticity and other valuable properties unimpaired. The subject has engaged the attention of a number of chemists, and different methods proposed, some of which are at present employed.

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* Journal de Physique, tom. xvii. p. 274.

† Annales de Chimie, tom. xi. p. 230.

Macquer having discovered the solubility of caoutchouc in ether, supposed that advantage might be taken of this, so as to apply it to these purposes: the concentrated solution being applied on a mould in successive layers, each layer being allowed to dry before another was laid over it. This method, however, is too tedious and expensive to admit of being much used.

The solutions of it in oils, can scarcely be employed in this manner, as the inspissated caoutchouc always remains clammy, and cannot be rendered perfectly dry. Dr Roxburgh found, however, that the solution of it in what has been named Cajeput oil, obtained by distillation from the leaves of the Melaleuca leucadendron, dried perfectly without any remaining clamminess; so that "a piece of catgut, covered with the half inspissated solution, and rolled between two smooth surfaces, soon acquired a polish and consistence very proper for bougies*."

Grossart, in a memoir on this subject†, proposed a method in which the caoutchouc was not fully dissolved, but merely softened so far that it adhered. A common bottle of it was cut into a thin slip, and this was macerated in sulphuric ether until it was softened. It was then removed, and rolled spirally round a mould, taking care to press with the hand the sides of it closely together, and compressing the whole by a slip of tape and thread. A hollow tube was thus formed on the mould, and if this was made a little conical, it was easily withdrawn: or this was facilitated by plunging the whole in warm water, which softened and expanded the caoutchouc. To lessen the expence, Gossart employed oil of lavender, or oil of turpentine, instead of the ether, and found that either of them answered sufficiently well; a longer time only being requisite to have the tubes perfectly dry and firm. And in prosecuting these researches, he found, that the same purpose was attained merely by warm water; which, proceeding in the same method as with the ether, softened the slip of caoutchouc so completely, that its sides formed a perfect adhesion. This is the method now generally followed, I believe, in the construction of instruments of caoutchouc. The following directions have been given for the management of the process, the heat being best applied by the medium of boiling water: "Split a stick of cane, and then apply together again the split pieces, but with a slip of whalebone interposed between them. Cut the elastic gum into slips fit for twisting over the prepared cane, so as to cover it; then, by duly heating the surface of the cane covered with the caoutchouc, it will melt so as to form one piece. When cold, draw out the interposed whalebone from between the split cane; by which means, without difficulty, the whole substance of the cane may then be readily withdrawn from under the covering, thus leaving the tube formed as desired *."

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* Nicholson's Journal, 4to, vol. iii. p. 439.

† Annales de Chimie. tom. xi. p. 143.

The solution of caoutchouc in some of the oils, has been used as a varnish, to render flexible substances, as silk, &c. impermeable to water or air. It has the advantage of being perfectly flexible, but it is long before it

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* Philosophical Magazine, vol. xxii. p. 340.

dries, and is liable to be softened by a very moderate heat. To render it less viscid, it is generally prepared from a mixture of volatile and expressed oil.

THE vegetable product which is known by the name of BIRDLIME, has in many of its properties, a close resemblance to caoutchouc, being like it possessed of great tenacity and elasticity, and having very nearly the same general chemical properties; so much so, that perhaps they may be regarded as varieties of the same principle.

Birdlime appears to be a natural production, and exudes spontaneously from certain vegetables, forming a viscid matter, which collects on their leaves or stems. It is thus secreted in considerable quantity by the Robinia viscosa. It is, however, generally extracted by an artificial process, which is, in some measure, kept secret. The following account of it is given by Geoffroy: "The inner bark of the holly is boiled in water seven or eight hours, till it become soft and tender. This is laid in masses in the earth, and covered with stones, placing one layer over another, the water having been previously drained from the bark. In this state it is left to ferment, during a fortnight or three weeks, in which time it changes to a kind of mucilage. It is then taken from the pit, pounded in mortars till reduced to a paste, washed in river water, and kneaded till freed from all extraneous matters. The paste is left in earthen vessels during four or five days, to ferment and purify itself. It is afterwards put into proper vessels, and thus becomes an article of commerce *." The same, or a similar substance, is prepared from other vegetables; as from the wild vine, and the different species of misletoe: and, as remarked by Lagrange, who has lately submitted it to chemical investigation, the birdlime of commerce is often a composition of the above preparation, with oil, turpentine, and other viscid substances. To obtain it pure, he prepared it from the inner bark of the holly, by a process nearly the same as that described by Geoffroy, and it is from his memoir † that the following account of its properties is principally taken.

It is of a greenish colour, and has a flavour somewhat acescent: its smell is similar to that of linteed oil: it is extremely viscid and tenacious; and when the hands are wet, so that it can be handled, it can be stretched out to a great length, and on withdrawing the stretching force, it gradually returns to its former dimensions. When stretched, its texture appears distinctly fibrous.

Spread on a glass plate, and exposed for some time to the action of air and light, it dries, becomes brown, and loses its viscosity, so that, when quite dry, it can be reduced to powder; but it recovers it on the addition of water.

It reddens the infusion of litmus, from the presence of a small portion of acetic acid, which is probably, however, foreign to its composition.

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* Nicholson's Journal, vol. xiii. p. 14

† Ibid. vol. xiii. p. 144.

When heated gently in a porcelain vessel, it melts, though without becoming very liquid, and swells in bubbles which rise to the surface: if the fusion be continued for some time, it acquires a brown colour; but on cooling, it recovers its characters. Placed on burning fuel, it burns with a bright flame, and the emission of much smoke; and it equally takes fire and burns when raised to a red heat in a crucible: a whitish residuum is obtained, which is very alkaline, and in which re-agents discover the presence of sulphate and muriate of potassa, and which contains also carbonates of lime and argil, with a small portion of iron.

Water has little action on birdlime. On boiling it in a quantity of water, it does not dissolve, but acquires rather more fluidity, which it loses, however, in cooling; and the water receives merely a slight impregnation of acid and of mucilage.

The action of the alkalis on it is energetic. Pure potassa forms with it a whitish magma, ammonia being at the same time evolved. This matter is less viscid than birdlime: it hardens from exposure to the air, and its taste and smell are similar to those of soap. It is almost entirely soluble in water and in alkohol as soap is, and is decomposed like it by the acids.

The acids likewise act on birdlime: when diluted, they soften and partly dissolve it; when concentrated, they decompose it. Sulphuric acid blackens it, evolves charcoal, and causes a formation of acetic acid and ammonia. Nitric acid in the cold has little effect on it; but, on applying heat, the mixture becomes yellow, the birdlime dissolves, and, as the evaporation advances, swells, leaving at length a hard brittle mass. This, by being again subjected to the action of nitric acid, is converted into oxalic and malic acids. Muriatic acid in the cold has no action on birdlime: when heated on it, it turns it black. Oxymuriatic acid produces on it very important changes, either by shaking the gas with the water containing birdlime, or by stirring it with the acid in a concentrated state: the birdlime lost its colour, and became white: it is no longer viscid, but in hard masses, containing in their central part a quantity of birdlime, to which the acid has not been able to penetrate; and it is also no longer fusible. These changes appear to be owing to the oxygenizement of the birdlime. Acetous acid softens birdlime, and dissolves even a certain quantity, the liquor acquiring a yellow colour.

A number of the metallic oxides are reduced when heated with birdlime. Oxide of lead forms with it a compound of the consistence of plaster.

Alkohol, when boiling, dissolves birdlime: the solution, while hot, is transparent, but becomes turbid as it cools; and a yellow matter may be separated by filtration, which is softer than the original mass, melts in a moderate heat, and diffuses an odour similar to that of wax, of the properties of which it appears to be possessed. The filtered liquor is bitter, nauseous, and acid; affording a precipitate on the addition of water, and leaving, on evaporation, a substance similar to resin.

Sulphuric ether is the proper solvent of birdlime: it dissolves it rapidly, and nearly entirely, leaving only any impurities. The solution is of a greenish yellow colour, and reddens infusion of litmus. On adding water to it, the mixture thickens, and the ether swims on the top: if a sufficient quantity of water is added to dissolve the ether, a quantity of oil is formed on the surface, having a considerable analogy to that of lintseed. By evaporating the solution of birdlime in ether, a greasy substance is obtained, of a yellow colour, and of the consistence of wax.

Some chemists have supposed birdlime analogous to gluten; and there are, no doubt, certain points of resemblance between them. It differs from it, however, as Lagrange has remarked, in being much less animalized; hence it is not liable to putrefaction, but can be preserved in water a long time without any sensible change: it differs also in the great quantity of resinous matter that may be formed from it by nitric acid, and in its solubility in ether.

It is much more analogous to caoutchouc, with which, however, it has not been usually connected. Like it, it is possessed of great tenacity and elasticity; is fusible; inflammable; affording much smoke in its combustion: it is insoluble in water, soluble in ether; and suffers changes somewhat similar from the acids, and even from the alkalis. It differs from caoutchouc, in being rather more easily acted on by these agents, in being soluble in alkohol, and in appearing to suffer rather more change in its constitution from these combinations. But these differences are not very considerable, and perhaps not greater than what may occur in varieties of the same species.

This conclusion receives, perhaps, confirmation from an observation made by Dr Roxburgh. The caoutchouc of the Ficus religiosus, the Ficus Indica, and the Artocarpus integrifolia, he found to be much less elastic than that from the Hævea or the Urceola, but much more viscid; while, in inflammability, and in their relations to the acids and other chemical agents, they are nearly the same. This fact, by proving that there are several varieties of caoutchouc, not perfectly uniform in their properties, and some of which appear to approach to birdlime, is sufficient, perhaps, to connect it with the species.

SECT. VIII.

FIXED OIL.

THE name of Oil is given in common to two vegetable proximate principles, which agree in the possession of a number of properties, but which likewise differ so far, that they must be regarded as essentially distinct. One of these species of oil is volatile at a high temperature; the other cannot be volatilized without decomposition; hence they may be distinguished by the epithets Volatile and Fixed. The volatile have also been named Essential Oils,—the fixed, Expressed Oils, as it is by the process of expression that they are usually obtained. The chemical history of expressed oil is to be the subject of this section.

These oils are formed abundantly in the vegetable system: they are contained generally in the seeds and fruit, and are found only at the period of maturity, or, at least, are found then in largest quantity. They are extracted, in general, by expression; the fruit, or the seeds bruised, being subjected to pressure in a hempen bag inclosed in a press, and any foreign matter forced out with the oil being allowed to subside. In this way are prepared the oils from the fruit of the olive, and the seeds of the almond. The process is facilitated by the application of heat, or by even previously roasting the seeds gently, especially with regard to those seeds which contain much mucilage: but from this the oil generally acquires some acrimony and empyreuma; it is even so far changed in its qualities, as to be less liable to congeal, and more disposed to become dry or solid when exposed to the air. Oils prepared in this manner are therefore named Drying Oils; and from these changes, the process is applied only to the extraction of the coarser oils, as those of lintseed or rapeseed. Sometimes, too, oil is extracted by decoction, the seeds being bruised, and boiled in water, the oil separating, and swimming on the surface. In this way is prepared what is named Castor Oil, from the seeds of the Ricinus communis.

The oil which is extracted by either process frequently has an impregnation of extractive, resinous, or other foreign matter, whence it derives taste, flavour, and, in some cases, more active qualities. The oils of olives and of almonds are the purest met with in commerce, and appear, indeed, to be perfectly free from any foreign impregnation. Oils less pure, but in larger quantity, are procured for the purposes to which they are applied in the arts, from lintseed, hempseed, rapeseed, from the nuts of the beech mast, and from the seeds of a number of other plants.

Fixed oil is fluid at moderate natural temperatures: by no great reduction of temperature, however, the different kinds of it are congealed, some of them even at a temperature not so low as the freezing point of water; and there are others, as the oil of the cocoa nut, of the laurel berry, or of the nutmeg, which are always concrete, whence they have obtained the name of Vegetable Butters.

Fixed oils, when liquid, are always somewhat thick and viscid, but, when pure, perfectly transparent: they have also the property named unctuosity: they are colourless, or of a yellow or greenish tinge: they are insipid, or have a very mild taste. They are lighter than water, and hence swim on its surface. They are altogether incapable of combining with water, as, even when strongly agitated with it, the globules of oil, when the agitation ceases, soon separate, and collect at the surface. They are equally insoluble in alkohol.

Though the fusibility of these oils is such, that they are usually fluid at natural temperatures, yet they cannot be volatilized without decomposition; and even this requires a high temperature. In general, they do not boil at a heat less than about 600° of Fahrenheit; and when the operation is conducted in close vessels, so as to condense this vapour, the qualities of the oil are found to be changed: it has lost its insipidity, has become more acrid, and, by repeated distillations, it becomes more light, limpid, and volatile, acquiring, at the same time, an empyreumatic odour, and becoming soluble in alkohol. When this distillation is carried on with a very strong heat, a quantity of carburetted hydrogen, of carbonic acid, and of an acid liquor, are produced along with the empyreumatic oil; and there is a residuum of charcoal.

Expressed oils are altered by exposure to the atmosphere, especially at a high natural temperature: they acquire a sharp taste and a disagreeable smell, and become thick. This change is termed Rancidity: it is owing to the absorption of oxygen which always accompanies it, as Berthollet had long ago demonstrated *. The oxygen appears sometimes to combine with the entire oil; in other cases, it is said to unite with part of its principles, and form an acid, the Sebacic, which is diffused through the rest of the oil, and is the cause of the change in its properties; and there is also a portion of water slowly formed. When the oil is exposed to pure oxygen gas, the same change takes place still more speedily; and some absorb a large quantity. Lintseed oil, it is stated by Saussure, absorbed, in his experiments, more than twelve times its volume of oxygen gas in the space of four months †, and this without forming any carbonic acid. Drying oils, or those extracted by expression with the assistance of heat, it has already been remarked, do not become rancid from exposure to the air, but, by the absorption of its oxygen, are rather converted into a resinous matter, especially when exposed under a thin and extensive surface.

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* Mémoires de l'Acad. des Sciences, 1785, p. 329.

† Recherches sur la Vegetation, p. 154.

It appears, from well-established facts, that this absorption of oxygen by fixed oils may, under certain circumstances, be so rapid, as to produce a temperature sufficient to cause them to burn. Many instances of spontaneous combustion had from time to time occurred from this cause, and, in particular, had been so frequent in the Russian navy and arsenals, that at length a series of experiments on the subject was ordered to be instituted; and from these, the circumstances connected with the fact have been fully ascertained. It appears, that if hemp, flax, or linen cloth, be steeped in lintseed oil, if it lie in a heap, and be somewhat pressed together and confined, its temperature rises, a smoke issues from it, and at length it takes fire. The same thing happens, with mixtures of oil with fine charcoal, as lamp-black, wrapt up in linen. In one experiment, a mixture of this kind became warm in about sixteen hours, and emitted steam; in two hours more, it emitted smoke, and immediately afterwards took fire. In another, the combustion happened in nine hours. The experiments succeeded only when drying oils were used *.

At the same temperature nearly at which oil is volatilized, it combines with oxygen with rapidity, so as to produce the phenomena of combustion, or to extricate a large quantity of light and heat. For this purpose, the oil must be converted into vapour, and its temperature raised even to ignition. Hence is derived the utility of a wick in supporting its combustion. The wick, made of cotton or any other material consisting of slender threads, draws up a portion of the oil by capillary attraction. By kindling the

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* Repertory of Arts, vol. iii. p. 95.

wick, the portion of oil it contains is converted into vapour, and ignited. As fast as it is consumed, a new supply is afforded by the same capillary attraction. The oil consists principally of carbon and hydrogen: the hydrogen requires rather a lower temperature for its combustion than the carbon does; hence the combustion of oil in atmospheric air is attended with a black smoke, which consists of the light carbonaceous matter suspended in the current of hot air. Where the air has not sufficient access to the wick, this smoke is very abundant; and it may, on the contrary, be entirely removed, by increasing the current of air, so as to render the combustion more rapid. This is done, for example, in Argand's lamp. It consists of a hollow wick, through the internal part of which a free circulation of air is established. When the wick is kindled, the air within it is immediately rarified; a strong ascending current is thus formed; fresh atmospheric air is rapidly brought into contact with the burning oil; the combustion is thus rendered more rapid, and thus so much caloric is extricated, as to keep the temperature of the oil so high, that all the carbon of the oil is consumed. Hence the combustion in these lamps is attended with no smoke; and from a given quantity of oil, more light and caloric are extricated, as the whole of that oil is consumed. There is reason to believe, that in the volatilization of the oil by the ignited wick, it is decomposed, and converted principally into that variety of carburetted hydrogen named Olefiant Gas, which we know, when pure, burns with precisely the dense oily-like flame that ignited oil does.

The products of the combustion of oil are water and carbonic acid. Lavoisier examined this combustion particularly. He found, that 100 parts of olive oil, during their combustion, combine with 321 parts of oxygen, and produce 140 parts of water, and 281 of carbonic acid. Hence he inferred, that oil consists of 79 parts of carbon, united with 21 of hydrogen. His conclusion, however, was founded on two suppositions, neither of them just,—that common charcoal is pure carbon, and that no oxygen exists in the composition of the oil: the proportions of carbon and hydrogen must therefore be regarded as mere approximations; and oxygen must probably also be admitted as a constituent principle of oil. That it is so, appears to be established by the decomposition of oil in close vessels; when transmitted through an ignited tube, carbonic acid and water are part of the products.

The expressed oils suffer decomposition from the action of the greater number of the acids; with phenomena, however, somewhat different according to the nature and concentration of the acid.

Sulphuric acid almost immediately renders oil brown, and at length black, by evolving part of its carbon in the state of charcoal: a portion of water has been also affirmed to be formed; and the formation of sulphurous acid is discovered by its pungent smell. If heat be applied, the action becomes more rapid, and the mutual decompositions more complete: and with certain proportions, the whole even of the oxygen of the acid may be abstracted, and sulphur obtained.

The action of nitric acid on oil, is less violent: the oil is merely thickened and rendered white: when heat is applied, or when the oil is heated previous to the addition of the acid, the action is more rapid, and nitrous acid vapour is disengaged. The action is more rapid on the drying oils, a resinous-like matter being formed: and if heat be applied, there is a violent effervescence, and the oil may even be inflamed, by the acid.

Muriatic acid has very little effect, when mixed with the oil in the cold: but according to Cornette, if the mixture is kept a long time in digestion in a sand heat, the colour of the oil darkens, and it becomes at length black *. By distillation the acid passes over with little change. The oxymuriatic acid causes nearly the same changes in the expressed oils, as the nitric; thickening them and rendering them white.

The other acids exert very little action upon expressed oil.

With the alkalis, expressed oils form a chemical combination: the product is the well-known substance Soap, in which the properties both of the oil and alkali are considerably modified.

If one part of a pure expressed oil, of that of olives for example, be mixed with half its weight of the common potash ley, a combination is effected between them: the oil becomes much thicker and white, and the acrimony or causticity of the alkali is much lessened. The compound, too, is to a certain extent capable of combining with water: a perfect solution indeed does not take place, but an opaque milky mixture is formed, from which the oil does not separate for a considerable time.

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* Mémoires de l'Acad. des Sciences, 1780, p. 563.

In this mixture, however, the combination of the oil with the alkali is very imperfect. It is rendered much more complete by the assistance of heat, or by boiling them together. One part of carbonate of soda is dissolved in 8 or 10 parts of water, and quicklime is added to abstract the carbonic acid : the liquor is filtered, and evaporated so far that its specific gravity shall be to that of water as 11 to 8. One part of this ley is mixed with two of an expressed oil, of that of olives for example, and the mixture is exposed to a moderate heat, sufficient only to make the liquor simmer. It is agitated constantly. An intimate combination of the oil and alkali takes place : the heat is continued till on allowing a few drops of the liquor to fall on a stone, it congeals, and the water separates from it. It is then removed and cast in moulds.

This is the process for preparing the finer kind of soap. The coarser soaps, which are in common use, and are manufactured on a large scale, are prepared from less pure materials; and the process which is followed, is somewhat different from that above described. An elaborate report was presented on this subject, by Pelletier, Darcet, and Lelievre * ; and the account of the manufacture of soap which follows, is principally taken from their memoir.

The oily matter which is employed in the fabrication of common soap, is different in different countries. In France, the coarser kind of olive oil is used ; and, accord-

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* { Mémoires de Chimie de Pelletier, tom. ii. p. 249.
Annales de Chimie, tom. xix. p. 253.

ing to the report of the French chemists, it forms the best soap. In this country, animal fat is generally employed; and, according to the same authority, it is next to olive oil that which gives the best hard soap.

The alkali which answers best, is soda: it forms a soap which easily becomes concrete, while potassa forms one that always remains soft. In countries, therefore, where barilla can be obtained at a low price, it is used in the preparation of soap. In this country it would be too expensive: the potash of commerce is therefore used: and in order to render the soap sufficiently disposed to congeal and become hard, there is added towards the end of the boiling of the alkaline ley with the unctuous matter, a quantity of sea salt; the soda of which being in part evolved by the potassa, produces this effect.

The alkali must of course be in its pure, or what is named its caustic state: whether barilla or potash, therefore, be employed, the carbonic acid combined with the alkali in either of them, is abstracted by lime, and the solution thus obtained forms the soapmakers' ley. When barilla is employed, after being reduced to coarse powder, it is mixed with the lime: the proportions used being 5 lbs. of barilla with 1 of lime. The mixture is put into a large wooden trough, with such a quantity of water as will cover it several inches: it is stirred; and after it has stood some hours, the ley is withdrawn, and is named the First ley: it is of such a specific gravity, that a fresh egg does not sink in it. A new quantity of water is poured on the materials, and after some hours is drawn off, affording a weaker ley. This is repeated once or more, forming a third ley: and, lastly, the residuum is washed with water, which now receives so slight an impregnation, that it is reserved only for adding to a fresh quantity of the materials.

The proportion of oil that is requisite, is 6 parts, when 5 of barilla and 1 of lime have been used. To combine them, they are to be boiled together; the boiler is a large iron pot fixed in a brick furnace, there being adapted to it a crib of wood: the oil is put into this boiler, with a portion of the weakest or third ley, and heat applied, so as to cause the mixture to boil: fresh portions of the ley are added from time to time, until the whole is consumed: the second or stronger ley is added in the same manner; the mixture being well stirred: the oil now becomes of a milky appearance, it unites perfectly with the ley; and after some hours of boiling, the mixture becomes more uniform, and acquires a thicker consistence. A small portion of the first ley is then added, and it is still carefully stirred, and kept boiling. The successive addition of small portions of the first ley, thickens the mixture: the heat is continued for some time, until it become more and more thick, and the soap now formed begins to separate from the watery liquor; a small quantity of sea salt is then added, which renders the separation more complete, by attracting the water: the boiling is continued for two hours longer; the fire is then withdrawn, and the whole allowed to remain at rest. In a few hours the soapy matter collects towards the surface, and the watery part subsides: this last is drawn off by a tube at the bottom of the boiler: the fire is then again applied, a small quantity of water or of weak ley being added, to facilitate the liquefaction of the soap. The mixture being perfectly liquefied, and being brought to ebullition, the remaining part of the strong ley is added in small quantities. The congelation of the soap can now be discovered: this is judged of, by withdrawing a small portion, which is allowed to cool on a plate of glass; and by the degree of consistence ~~which is acquired~~, it is determined if the preparation be complete. If it be so, the fire is withdrawn; the soap is left at rest for some hours; the liquid beneath is withdrawn by the stop-cock: the fire is again applied, a small quantity of water being added to promote the liquefaction; and when the whole has cooled a little, it is run into the vessels in which it is to congeal, in the bottom of which a little lime in powder is equally strewed. After some days, the soap has become sufficiently firm to be cut into the form under which it is usually sold.

Though such be the general outline, it is no doubt varied by different manufacturers, and in different countries; but by following this process, a soap of excellent quality may be formed. In this country, as has been already observed, the principal difference is in using animal fat, to which, in forming yellow soap, a portion of resin is added; and in using potash instead of soda. From the latter variation, it is necessary to use muriate of soda in larger quantity than when barilla is employed, in order to afford a portion of soda, to render the soap concrete. The French chemists, in their experiments on soap, found, that when they substituted a ley from potash for that from barilla, using the same oily matter, and observing the same process in every other respect, they obtained only a soft soap. But if they added, in the course of the boiling, a solution of muriate of soda, they obtained a soap perfectly firm: or if they began the process with a ley of potash, and finished it with a ley of soda, they ~~had~~ the same result.

The veined or marbled soap, as it is named, differs from the other merely in its streaks of colour, and in being prepared from the purest materials~~, as it is used~~ for medicinal purposes. The variegated colour is given to it, by adding to the soap when nearly fully boiled, a small quantity of fresh alkaline ley, and soon after a solution of sulphate of iron; black oxide of iron is thus precipitated, which, from the action of the soap, assumes a blue tinge. Brown or red oxide of iron is then diffused in water, and stirred through the soap, so as to be mixed with it in streaks. This soap is also more solid than the other, as in the operation the water is more effectually dissipated.

The soft soap of commerce is prepared from the common potash, rendered caustic by lime, and boiled with some of the coarser oils, as of rape-seed, hemp-seed, or lint-seed, or even with fish oil.

Some observations have been added by Pelletier, Darcet, and Lelievre, on the adulteration of soap frequently practised. The most common method is to cause it to imbibe a large quantity of water; and to prevent the dissipation of this from exposure, those who practise it keep the soap in a saturated solution of muriate of soda. This is detected by the great loss of weight which such soap sustains from exposure to the air. Other modes are also said to be practised, as by the addition of chalk, clay, alum, sea salt, and other substances.

These chemists executed the analysis of soap. When properly prepared, 3 lbs. of oil ought to furnish 5 lbs. of soap: but from this it is not easy to discover, at least with perfect accuracy, what proportion of alkali and what quantity of water it contains. The proportions they assign are, in 1 lb of soap, 9 ounces 6 drachms of oil, 1 ounce 3 drachms of pure alkali, and 4 ounces 7 drachms of water.

The cleansing property of soap depends entirely on the alkali it contains: the alkaline power is no doubt partly impaired by the combination; and hence it might be supposed more economical, to use merely the alkaline solution. In some cases it is so, as in some of the steps [illegible] the process of bleaching; but for common use, soap has some advantages; as it acts less on the fibre of the cloth, and gives to it a softness and smoothness, which the alkali alone would not do.

Soap is soluble in water; but the solution is always in a certain degree opaque, owing perhaps to particles of uncombined oil being present. It is likewise soluble in alkohol; and if the purest soap has been employed, this solution is nearly transparent; if strong, it is of a gelatinous consistence.

Soap is decomposed by all the acids, which attract its alkali, and separate its oil. The greater number of the neutral salts, either earthy or metallic, likewise effect in it the same decomposition. This is the reason that, with what are termed Hard waters, a proper solution of soap cannot be formed,—the sulphate of lime contained in the water decomposing the soap. The solution of soap, therefore, in alkohol, is a very convenient test for discovering these salts in water. In these cases of decomposition by the earthy and metallic salts, the oil which is separated combines with the earth or metallic oxide. When this oil, however, is separated by an acid from the soap, it is affirmed, that in several respects its properties are altered; and that, in particular, it is now soluble in alkohol. During its conversion into soap, therefore, it must not merely have combined ~~with the alkali~~, but have further undergone some chemical change. It has been supposed to receive oxygen from the air.

When soap is exposed to heat in close vessels, it affords oil, water, and a portion of ammonia. The origin of the [illegible]t product is not very evident, since oil is supposed to consist only of carbon, hydrogen, and oxygen; but perhaps it may be obtained only from soaps that have been formed in whole or in part from animal fats, in which a portion of nitrogen may exist.

Ammonia acts upon the expressed oils in a manner similar to the fixed alkalis, forming with them a saponaceous compound, which is thick and white, and which is also diffusible in water; hence it is used in pharmacy, to render oils miscible with water. The combination, however, is much less intimate than that with the other alkalis, as heat cannot well be applied to render it perfect. Berthollet discovered an indirect process by which a proper ammoniacal soap may be formed. It consists in mixing a solution of common soap with a solution of muriate of ammonia: the muriatic acid is attracted by the alkali of the soap, and the oil combines with the ammonia, forming a kind of coagulum. This soap is much less soluble in water than common soap, has a more pungent taste, is less consistent, and is decomposed by long exposure to the air. It is soluble in alkohol.

Berthollet, in a memoir on the combinations of oils with earths and metallic oxides *, has described the properties of the saponaceous compounds thus formed, and the processes by which they may be obtained.

Lime-water acts upon expressed oil nearly in the same manner as an alkaline solution, forming a white and thick mixture; but the proper calcareous soap is formed either by mixing a solution of soap with a solution of sulphate, muriate, or nitrate of lime, or by adding it to lime-water: the lime unites, in either case, with the oil of the soap, and forms a combination which is sparingly soluble, and which remains on the filtre.

By a similar process, Berthollet formed magnesian and argillaceous soaps,—adding, to form the one, a solution of sulphate of magnesia; to form the other, a solution of alum to a solution of common soap. The magnesian soap was of the utmost whiteness, unctuous, dried with difficulty, and preserved its white colour after exsiccation. It melts with a moderate heat, and forms a transparent mass, slightly yellow, and very brittle: it is insoluble in boiling water, but alkohol dissolves it; when water is added to the solution, it becomes milky. The argillaceous soap was soft and tenacious, and preserved its tenacity in drying: it melts readily, and exhibits, after fusion, a mass of a beautiful transparence, rather yellow. It appeared to be insoluble in water, alkohol, or oil.

The solution of muriate of barytes afforded, with soap, a combination nearly the same in appearance and properties as the soap of lime.

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[*] Memoires de l'Acad. des Sciences, 178
Nicholson's Journal, 4to, vol. i. p. 170

Combinations of expressed oil with metallic oxides can be formed by a similar process,—adding to a solution of soap a solution of a metallic salt; and the properties of a number of these compounds have been examined by Berthollet. The combination formed in this manner with oxide of mercury, he found to be viscid; to dry with difficulty, losing its white colour in drying; to be soluble in oil, and very sparingly in alkohol. That with silver is at first white; but after a few moments' exposure to the air, it becomes red: that of gold, which is also at first white, soon assumes a purple colour; these changes of colour in these combinations being no doubt owing to the facility with which their respective metals part with oxygen. The combination with oxide of iron is of a reddish brown colour, tenacious, and easily fusible: that with copper is of a green colour: when digested in alkohol, its colour becomes deeper, and it liquefies, but does not dissolve in the cold: ether renders its colour deeper and more beautiful, and dissolves a considerable quantity of it: it is also abundantly soluble in oils, to which it gives a fine green tinge. This, on account of its solidity and its fine green colour, has been proposed to be used as a paint *. The compound which oxide of lead forms is white, tenacious, and very adhesive when heated: that of tin is also white: it is not, like the other metallic soaps, fusible; but is decomposed by heat. The soap of zinc is yellowish white, dries speedily, and becomes fusible: that of cobalt is of a dull leaden colour, and dries with difficulty; and

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* Journal de l'Ecole Polytechnique, Cah. iii. p. 427.

that of manganese white, but, on exposure to the air, assumes a peach-bloom colour, which gradually deepens *.

Expressed oil is capable, too, of acting more directly on some of the metallic oxides, and even of promoting the oxidizement of some of the metals. If copper be rubbed over with grease, and exposed to the air, the surface soon becomes quite green, the fat probably absorbing oxygen, which acts on the metal. The oxidizement of mercury by trituration with lard probably depends on the same agency. With oxide of lead, expressed oil combines very readily, either by trituration, or in a more perfect manner by boiling; and by the last method, so much of the oxide is dissolved, that the compound, when cold, assumes a solid consistence, and is hard. This forms what in pharmacy is named Common Plaster, prepared by boiling two parts of oil with one part of vitrified oxide of lead (*litharge*), adding a small of portion of water to prevent the composition from being scorched. The mixture becomes white: it retains this whiteness when cold, but becomes yellow from long exposure to the air. Its texture is somewhat foliated, and it is easily melted. From its adhesive quality and its mildness, it is well adapted to the uses to which it is applied in surgery. Deyeux, who has made some observations on these combinations †, has remarked, that some other metallic oxides, as those of bismuth and mercury, may be made to afford similar compositions with oil.

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* Nicholson's Journal, 4to, vol. i. p. 172.

† Annales de Chimie, tom. xxxiii. p. 30.

Expressed oil is capable of combining with sulphur, by boiling them together. This solution, named in the shops Balsam of Sulphur, is of a dark reddish brown colour, an extremely fœtid smell, and an acrid taste. By the application of heat, it emits sulphuretted hydrogen. When concentrated, sulphur is deposited from it, crystallized in octaedrons.

Expressed oil is also capable of dissolving, with the assistance of heat, phosphorus in small proportion. The liquid is luminous, when exposed to the air and rubbed. When saturated, a part of the phosphorus is deposited, on cooling, in octaedral crystals.

It unites with several of the other vegetable products; with gum, fecula, and sugar. If triturated with any of these, and a little water, it forms a milky fluid, which may be diffused through water without the oil immediately separating. The mucilage suspends it more completely than either of the others; and it is frequently used in pharmacy for this purpose. The mixture with it is milder than that in which the oil is mixed by a small quantity of alkali; but it is also less permanent.

Expressed oils are applied to many purposes in the arts. They form the basis of paints, the oil being triturated with white oxide of lead, and the colouring matter being afterwards added. Combined with resin and turpentine, they form what are named Fat Varnishes, which differ from the spirit varnishes in being, when dry, more flexible. Mixed with lamp-black, they form the composition used as printing-ink. For these uses, the drying oils, those of lintseed, of poppy, hemp, or nuts, are employed; and they require even preparation. Not only is the seed from which they are extracted previously roasted, but the oil is boiled strongly for some time, is even sometimes kindled, and allowed to burn for a little, or is boiled with a small portion of litharge; and, for different purposes, these processes are often varied.

SECT. IX.

WAX.

THIS substance, though apparently formed by the Bee, has been regarded by chemists as a product of vegetation; and it is undoubtedly secreted by certain vegetables, forms a kind of varnish on their leaves or stems, or is mixed with their juices. Even that which is applied by the bee to the formation of its cell has been supposed to be simply collected by that insect from flowers, and, in particular, to be derived from the pollen, or fine dust of the antheræ, which undergoes a slight elaboration in the body of the animal, so as to acquire that tenacity which fits it for the purpose to which it is applied. This opinion, however, as to the origin of bees-wax, has been rendered doubtful, or rather perhaps has been disproved, by the experiments of Huber. He has shown, that bees form wax when they are denied all supply of the pollen of flowers, when they were confined to the hive, and supplied only with honey, or with sugar; and to obviate all source of fallacy, the comb previously formed was all removed from the hive, and the bees were confined for such a period, as that no quantity of pollen which they could have been supposed to have collected previous to their confinement could have possibly furnished the wax they formed. The honey or the sugar, too, always disappeared as the wax was formed ; and, on the other hand, bees confined, and supplied only with fruit and the pollen of flowers, formed no wax whatever. These facts appear to prove, that the pollen of plants is not the source of the wax which bees produce, but that it is formed from their saccharine food, by some changes to which this is subjected *.

Notwithstanding this conclusion, however, there is still reason to regard wax as being likewise a product of vegetation. It is the substance, according to Proust, which forms the silvery-like down on the surface of the leaves, flowers, and fruit of certain vegetables ; and it also exists, as he affirms, in the fecula of certain plants, as in that of the house leek, or the green cabbage †. And there are vegetables which even afford it in large quantity in nearly a pure state. Such particularly is the plant named Myrica cerifera, or wax-tree, a native of Louisiana. The seeds of this vegetable are encrusted with a white rough anylaceous-like substance, which, when rubbed between the fingers, feels unctuous. When they are boiled in water, it is melted off, and swims on the surface. This substance has been examined by Dr Bostock ‡ and Mr Cadet ||, and appears, from their experiments, to have near-

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* Nicholson's Journal, vol. ix. p. 182.

† Ibid. vol. v. p. 26.

‡ Ibid. 8vo, vol. iv. p. 129. || Ibid. p. 187.

ly all the properties of bees-wax. It is concrete; of moderate hardness; has in part the tenacity of bees-wax, but without its unctuosity; is like it inflammable; and exhibits the same general relations to chemical agents. Some of its physical properties are a little different, as its colour and smell; and it is rather more fusible, and somewhat more soluble in ether: but these are differences not at all essential, and such as cannot prevent it from being regarded as a variety of the same species. Cadet has observed, that there are other species of myrica which afford a similar product; and that other plants, as the Croton sebiferum, the Tomex sebifera, the poplar, the alder, and the pine, yield by decoction a concrete inflammable matter, more or less resembling wax.

The substance which has been described by Dr Pearson under the name of White Lac, from India, appears extremely similar to this *. A wax perfectly resembling that of the wax-tree is also obtained from common lac, in which it exists combined with resin, colouring matter, and a small portion of gluten; and is extracted by boiling in nitric acid, which dissolves the other principles, leaving the wax undissolved. And although this is an animal production, being the nidus of the Coccus or Chermes lacca, yet, as Mr Hatchet in his analysis of this substance remarks, it possesses few of the characters of animal substances; and the greater part of its properties, as well as of its component ingredients, are such as more immediately appertain to vegetable bodies †. From these

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* Philosophical Transactions, 1794.

† Ibid. 1804.

facts, it may be concluded, that wax is a product of the vegetable system; and though also formed by some animals, that, on the whole, it may with propriety be classed among the vegetable principles. In its chemical nature, it obviously approaches nearly to the fixed oils.

Wax, taking the variety prepared by the bee as that best known, is a solid substance, brittle at a low temperature, but acquiring tenacity when very slightly heated, so that it can be moulded into any shape. It is tasteless, and, when pure, nearly inodorous. Its colour is usually yellow; but this appears to arise from the presence of some foreign matter, as it can be deprived of it, and be rendered perfectly white, without any change in its properties. The bleaching of this wax, as this process is named, is performed by melting and running it into thin plates, which are exposed to the air, dew, and sun, until the colour is discharged. The wax of the Myrica cerifera, which has a greenish colour, may likewise be rendered white by bleaching.

Wax melts at a temperature of 142° of Fahrenheit, (white wax at 155°) *; and in cooling, passes through an intermediate state of softness to perfect solidity: the myrtle wax is rather more fusible, melting at 109°. Like the fixed oils, it is incapable of being volatilized without change. It affords vapour, however, when heated to ignition, consisting of its elements in a state of new combination; and this vapour, when the air is admitted, burns with a clear and white flame. Hence the use to which wax is applied in affording artificial light. The products

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* Memoir by Mr Nicholson, Journal, 4to, vol. i. p. 70.

of its combustion, like those of oil, are water and carbonic acid. From the quantities of these produced in the combustion of a given quantity of wax, Lavoisier inferred, that it consists of 82.28 of carbon, and 17.72 of hydrogen,—an inference which can by no means be regarded as accurate. When decomposed in close vessels, so as to collect the products, these are found to be a large quantity of thick and empyreumatic oil, a portion of water sensibly acid, carburetted hydrogen gas escaping, and a small portion of charcoal remaining. From this analysis, it must be regarded as containing oxygen as well as carbon and hydrogen in its composition.

Wax is insoluble in water, and equally so in alkohol, at least at a low temperature. Dr Pearson found, that alkohol, by digestion on it, at a temperature of 140°, dissolved a quantity; and Dr Bostock has found, that when it is boiled on wax, it dissolves a quantity, amounting to about a twentieth of its weight, the greater part of which is deposited as the alkohol cools. A small portion, however, still remains dissolved, which may be precipitated by water. The myrtle-wax is rather more soluble than bees-wax. Both are also dissolved by boiling ether, but the myrtle-wax in larger proportion than the other; and the greater part dissolved by this fluid is likewise deposited as the temperature falls.

The action of the alkalis on wax is somewhat similar to that on the expressed oils; the combination taking place, however, more slowly, and only when the alkaline solution is boiled on the wax. Dr Bostock, in his experiments on the wax of the Myrica cerifera, found that a soap is thus formed, which is sparingly soluble in cold water, and therefore separates in flocculi as the liquid cools: in this the wax has lost its fusibility and inflammability, and the compound is decomposed by the acids, the wax re-appearing with nearly its original properties. The action of the alkali on bees-wax is nearly the same, but rather less complete. A compound of this kind with bees-wax forms the Punic wax of the ancients, which has been used as the basis of colours, and in encaustic painting. Ammonia boiled on wax forms with it also a white saponaceous compound, soluble in warm, but very sparingly soluble in cold water. On vegetable wax, its action is more energetic than on bees-wax.

The acids act on wax with still less force than on the fixed oils, owing, no doubt, to its state of cohesion. Sulphuric acid, when its action is promoted by heat, is blackened by it, and at length dissolves it, forming a thick dark-coloured mass. According to the experiments of Beckman, when boiled in diluted nitric acid, it is whitened and hardened; and oxymuriatic acid has been proposed to be used in bleaching it. Muriatic acid has scarcely any action on it.

It is dissolved very readily by the fixed oils, when a moderate heat is applied, and forms a compound of an intermediate consistence, more or less firm therefore, according to the proportions. Such compositions form ointments and cerates in pharmacy. It is dissolved likewise by the volatile oils, with the assistance of heat.

From the properties now enumerated as belonging to wax, it is evident that it approaches nearly to the fixed oils. The principal difference is in its firmer consistence, and in its relations to some of the chemical agents, particularly to the alkalis. It has been generally supposed to differ chemically from them, in containing a larger proportion of oxygen; though this is by no means clearly established.

The principal consumption of wax, is in obtaining from its combustion artificial light. A candle of wax is superior to one formed of any other unctuous matter, in not requiring to be snuffed; the wick burning down equally with the body of the candle, and hence the light is always clearer and more steady. The reason of this has been very well pointed out by Mr Nicholson. In a tallow candle, as indeed in every other, the wick takes up by capillary attraction, the portion of matter fused by the heat of the flame: but as tallow is very fusible, a large wick is required, else a quantity of the melted matter would run down the surface of the candle; and this large wick occupying the centre of the flame, where it is secluded from the air, is not itself burnt down, but gives a shadow always increasing as it lengthens. In a wax candle, on the contrary, the wax being much less fusible, a very slender wick is sufficient to draw up by capillary attraction, all the matter that is melted; it therefore obscures less the illumination, and at the same time, when it lengthens a little, being so slender and flexible it bends to one side, its extremity thus comes to be without the flame; it is therefore burnt by the current of air applied to it in its ignited state. Hence the flame is always clear, and the snuffing of the wick is performed as it were by the combustion itself *.

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* Nicholson's Journal, 4to, vol. i. p. 76.

SECT. X.

VOLATILE OR ESSENTIAL OIL.

THE Volatile, though agreeing with the fixed oils in unctuosity, inflammability, and some other properties, differ from them materially in others. They are volatile at a low temperature, and are quickly converted into vapour at the heat of boiling water, without being decomposed: they are soluble in a small proportion in water: they are still more soluble in alkohol, and they do not easily combine with the alkalis. They are in general odoriferous, pungent, and even acrid; and they are more highly inflammable than the fixed oils.

These oils are less abundantly diffused through the vegetable kingdom than many other proximate principles. There are many vegetables in which they cannot be discovered; and they do not exist in any considerable quantity but in the aromatic plants. In some plants the oil is confined to the flowers, the fruit, the leaves, or bark; sometimes it is contained in several of these parts, and in a few instances it is found diffused through every part of the plant. The quantity varies not only according to the age, but also according to the vigour of the plant; hence it is much dependent on climate, soil, and season.

It is remarkable, that though in general the odour seems to reside in the essential oil, yet there are some of the most odoriferous flowers, as the violet or jessamine, which yield scarcely any essential oil, though they lose their flavour by a gentle heat.

Some of the essential oils being contained in distinct vesicles, may be obtained by simple pressure. In this manner, essential oils are obtained from lemon or orange peel. More usually they are obtained by distillation. The general process to procure an essential oil, is to expose the vegetable substance to heat, along with a large portion of water, in the common still. The heat of boiling water is sufficient to volatilize the oil: it is therefore carried over with the aqueous vapour: both are condensed in passing through the spiral tube connected with the still: the water retains the taste and flavour of the plant, from having dissolved a small part of the oil; the greater part of it, however, separates, swims on the surface, or in a few cases sinks to the bottom, and is easily obtained pure. Hence the oils prepared in this way, are named Distilled Oils; and the waters impregnated with them, Distilled Waters. When the process is conducted on a large scale, and with the sole view of procuring the oil, the same water is repeatedly used; as when impregnated with the oil in one distillation, it dissolves no larger portion, and the loss from this source is avoided.

The essential oils are in general lighter than water; though a few produced from the aromatic plants of hot climates, as cloves or cinnamon, are heavier: they are in general thin and fluid, though frequently also thick and viscid: some congeal at a very moderate reduction of temperature, others remain fluid at very intense colds. In congealing they assume a crystalline arrangement. A few oils are always obtained concrete, such as that of roses. Their colours are various, and each has a peculiar odour and taste; the odour is that of the vegetable from which it is extracted.

The essential oils are volatilized by a very moderate heat: if a greater heat is quickly applied to them, as when they are distilled without water, they suffer a change in their composition and properties; hydrogen is evolved, and charcoal is obtained as a residuum.

These oils exposed to the air, suffer a gradual change. They lose a great part of their smell; are thickened; and at length become nearly concrete: depositing at the same time, crystals of an acid nature. From these changes it was formerly concluded, that oils are not homogeneous in their composition, but consist of a subtle and volatile odorous matter, and of another more fixed; and that the changes the oil suffered from exposure to the air, were owing to the escape of the more volatile part. For this opinion there is no foundation; and these changes appear to arise from absorption of oxygen, which has been demonstrated by experiment: this appears to oxidize a portion of the oil, so as to form an acid similar to the benzoic; but the greater part of it, either by the loss of part of its hydrogen, or partly from this, and partly from the fixation of oxygen, is converted into a substance of a resinous nature. Water is also said to be formed in small quantity.

The volatile oils when heated, are inflamed even more easily than the fixed are, and their combustion is more rapid, owing probably to their greater volatility. The products of the combustion are water and carbonic acid. They yield more water than the fixed oils do; hence they consist of carbon and hydrogen, united perhaps with a portion of oxygen: and they differ from the fixed oils, in containing more hydrogen proportioned to their carbon. To this probably are owing their greater volatility and inflammability. Hence also, when fixed oils are exposed to heat, they are partially decomposed; part of the oil passes over, and a quantity of carbon is left in the vessel. By the separation of this carbon, the oil that has distilled over is found to have its properties altered, so as nearly to resemble the volatile oils: it is more volatile and inflammable, and is soluble in alkohol.

The essential oils are dissolved by water, but in very small quantity, only as much as communicates their flavour and taste. Distillation is not necessary for this combination being effected, mere agitation is sufficient; and thus waters may be formed, as strongly impregnated as those which are distilled.

The essential oils are much more soluble in alkohol; and this forms one of the principal distinctive characters between them and the fixed oils. Some appear to combine with the alkohol in every proportion, others in limited quantities; and there are some which are even sparingly soluble, as oil of lemon peel or of turpentine,—affording in common, with many other facts relating to the chemical relations of the vegetable proximate principles, a proof that in each the properties are not perfectly uniform, but exhibit gradations, undoubtedly from slight variations in the composition which constitutes the species. The solutions of the essential oils in alkohol, are decomposed by the affusion of water, which attracts the alkohol; the oil is separated, and being diffused through the fluid in minute globules, renders it milky.

The action of the acids on the essential oils, is more violent than their action on the fixed oils. Sulphuric acid blackens them instantly, and sulphurous acid and carbonic acid gases are disengaged with sudden effervescence and a considerable elevation of temperature. Nitrous acid acts with such violence, as often even to inflame the oil; and the inflammation almost always takes place when a little sulphuric acid has been added to the nitrous acid, immediately before its affusion on the oil. If the nitric acid be added more slowly, and with precaution to guard against inflammation, it appears from an experiment performed by Chaussier *, that prussic, malic, and oxalic acids are formed; the remaining oil is converted into a viscous resinous substance, and much carbonic acid, nitric oxide, and nitrogen gases are evolved, during the operation. The action of muriatic acid is less violent; it deepens in general the colour of the oil, and thickens it. The oxymuriatic converts these oils into a resinous-like matter.

The essential oils combine with difficulty with the fixed alkalis. By long trituration of the pure alkali with the oil, a combination is effected, and a saponaceous compound is formed; which is much less perfect, however, than that formed by the fixed oils with the alkalis, and generally decomposes on keeping. From the observations of Pelletier, it would appear, that when the alkali is saturated with carbonic acid, it combines more easily and per-

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Journal de l'Ecole Polytechnique, Cah. iv. p. 674.

fectly with the essential oils, than when it is pure: and he has supposed, that the indirect processes employed by the chemists to form these combinations, some of which were medicinally used, succeeded in consequence of the absorption of carbonic acid from the atmosphere *.

Liquid ammonia, distilled with the essential oils, dissolves them but very sparingly. It combines readily, however, with them when they are dissolved in alkohol.

These oils are capable of dissolving sulphur. The compound has an offensive smell and taste. From the saturated solution, part of the sulphur separates on standing in transparent crystals.

They likewise dissolve phosphorus; and from this saturated solution the phosphorus is also deposited in a crystalline form. Some of these solutions, that in oil of cloves for instance, are luminous, without giving out much heat.

They decompose some of the metallic salts, first attracting the oxide, from which the oxygen continues to be slowly attracted, probably by the hydrogen of the oil, so that the metal is at length precipitated in its pure form.

The volatile oils unite in some measure with mucilage or with sugar; and by the medium of either of these they may be suspended in water.

They are in general used as perfumes, or in the practice of medicine. Some of them enter into the composition of varnishes.

These oils are frequently adulterated, either by the ad-

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* Mémoires de Chimie, tom. i. p. 328.

dition of some cheaper essential oil, as that of turpentine, of a pure fixed oil, as oil of almonds, or of alkohol. The first is betrayed by its smell, when a little of the adulterated oil dropt on paper is heated before a fire, so as to volatilize it; the second by the oil dropt on paper leaving a greasy stain, even after the paper has been exposed to as high a heat as it can bear, and by not being soluble in alkohol; the third by becoming milky whenever it is mixed with water.

SECT. XI.

CAMPHOR.

Camphor is a principle of vegetables which in many of its properties resembles the volatile oils. Like them it is odorous, pungent, volatile, inflammable, sparingly soluble in water, and abundantly soluble in alkohol. It differs from them principally in its concrete form, in its peculiar odour, in its relations to the acids and alkalis, and the results of its decomposition by heat.

Camphor is a principle contained in many vegetables, especially the aromatic plants, and even those of our own country, as peppermint, rosemary, marjoram, and others: it appears to be volatilized in combination with their essential oil in the process of distillation, and, when these are long kept, is deposited in a crystalline form. Proust extracted it in this way in considerable quantity from oil of lavender, of sage, and other labiated plants; the first, by spontaneous evaporation, affording one-fourth; the second one-eighth of its weight: and he even supposed that it might thus be produced on a large scale. The process he followed with this view was to distil oil of lavender with the heat of a water bath inferior to 212°, until one-third had passed over; the remaining quantity when cold affords camphor, which may be separated from the adhering oil by pressure between folds of bibulous paper, and which, when refined by sublimation with a little lime, afforded a white concrete similar to common camphor, but retaining somewhat of the odour of the essential oil *. The same plants in this country, however, certainly do not contain any proportion of camphor, such as Proust describes; and it is even probable, that part at least of the camphor deposited from essential oils that have been long exposed to the air, has been actually formed from changes in the composition of the oil.

Camphor exists also in the roots of some aromatic plants, and has been extracted from those of cassia, cinnamon, and elecampane. The camphor of commerce is procured, however, from a particular plant, the Laurus camphora, a native of the East of Asia. It exists ready formed in the wood of this tree, can be seen interspersed through it in vesicles, and can be picked out. It then forms what has been named Native Camphor. It is usually procured, however, by the process of sublimation. The wood of the stem and branches, cut into small billets, is exposed with a little water to a moderate heat, in a kind of alembic, to the head of which is adapted a ca-

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* Annales de Chimie, tom. iv. p. 179.

pital in which straw is put. The camphor is volatilized, and attaches itself to the straw. It is a little impure, but is purified in Europe by a second sublimation.

The camphor of commerce, from its mode of preparation, is in the form of large semi-spherical cakes: when broken, it appears in fragments of a texture somewhat striated, having a degree of ductility, in consequence of which it can be compressed, and is not easily reduced to powder.; of a white colour, and semi-transparent; a little unctuous to the feel; having a very strong, peculiar, and rather fragrant odour, and a taste which is pungent and bitter. It is also susceptible of crystallization: when slowly sublimed, or when slowly precipitated from its solution in water by the affusion of alkohol, it appears in the form of acicular prisms.

Camphor, though a concrete substance, is even more volatile than the essential oils. It evaporates quickly at the common temperature of the atmosphere, losing in weight, and an angular fragment becoming spherical; and at a temperature between 100 and 150, it sublimes in close vessels unchanged. If heated under compression, or even if suddenly heated under the pressure of the atmosphere, it becomes fluid before it passes into vapour; and in the process of subliming it in the large way, the heat is so applied, that the camphor is kept fluid, and the sublimed cake is thus obtained more dense. The temperature at which it melts is, according to Venturi, 302° of Fahrenheit.

It is highly inflammable, kindles very readily, and burns with the emission of much light, and with a dense black smoke, which condenses into a smooth light charcoal.

Carbonic acid gas is produced, and a portion of the peculiar acid which has been named Camphoric Acid.

Camphor is very sparingly soluble in water. When triturated with it, it merely communicates its smell and taste to the water, which remains odorous, and somewhat pungent, even when filtrated; but no appreciable quantity is dissolved. A phenomenon which has excited some attention is presented, when pieces of camphor are placed on the surface of pure water. They soon begin to move with rapidity, and while moving dissolve, the solution taking place at the line where the water and the air are in contact; as is proved by immersing a cylinder of camphor in water part of its length: it becomes excavated, and at length is cut through, exactly on a level with the surface of the water; and the motions of the camphor are, according to Venturi, owing to this cause; or, as he has expressed it, the rotation of small pieces of camphor at the surface of water is the mechanical effect of the re-action which the oily liquor, (into which the camphor, by the solvent power of the air and water, is resolved), extending itself upon the water, exercises against the camphor itself *.

Camphor is abundantly soluble in alkohol: the solution is immediately decomposed, and the camphor precipitated in the form of a white powder, by the affusion of water; but if the water be very slowly added, and merely in such a quantity as to weaken the affinity of the alkohol to the camphor, the latter, in separating, presents a dendritic crystallization. It is also soluble in expressed and essential oils.

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* Nicholson's Journal, vol. i. p. 207.

The alkalis do not dissolve camphor, or produce on it any sensible change. Of the earths, magnesia appears to exert some action on it, as, when they are triturated together, the camphor is reduced to a smooth impalpable powder, which is easily diffused in water.

The action of the stronger acids on camphor is peculiar, and presents some singular results.

Sulphuric acid digested on it renders it brown; and at length a brown or reddish solution is obtained, from which, on the addition of water, camphor is again precipitated. This, however, it has been remarked by Mr Hatchet, in his late experiments on the formation of artificial tanin, takes place only at a certain stage of the process; and he has investigated other changes which happen with more precision. One hundred grains of camphor being added to one ounce of concentrated sulphuric acid, it gradually dissolved, forming a solution which, from yellow, deepened to a blackish brown; much sulphuric acid gas having been disengaged: at the end of two days, the production of this gas had ceased: the vessel was placed in a sand-bath, by which it was for a time renewed. At the end of two days more, six ounces of water were gradually added; a coagulum of a reddish brown colour was formed; the odour of sulphurous acid ceased, and was succeeded by one resembling that of a mixture of oils of lavender and peppermint. The whole was then distilled gradually: the water impregnated with this odour came over, accompanied by a yellowish oil, amounting to about three grains. When the whole of the water had distilled over, there was a slight production of sulphurous acid gas: two ounces of water were then added, and the distillation continued until a dry blackish brown mass remained: by the action of alkohol, part of this was dissolved, part remained undissolved: the latter, which amounted in quantity to 53 grains, had the appearance of a compact coal: the dissolved matter had the properties of tanin: it weighed, when obtained solid, 49 grains. Into these three substances, therefore, the camphor had been resolved, by the action of the sulphuric acid causing its elements to enter into new combinations, and perhaps imparting a little oxygen, as there was an increase of weight equal to 5 grains *.

The action of nitric acid on camphor is very different. In the cold it dissolves it, and the solution divides into two portions,—one a yellowish liquid of an oily-like appearance, which floats above the other that appears more watery. The first contains camphor in a state of solution in nitric acid, and is decomposed by the affusion of water: part of the camphor has, however, been changed in its composition; for not more than two-thirds of the portion operated on can thus be recovered: the remaining quantity appears to exist in the state of an acid, with a quantity of nitric acid in the watery fluid beneath. By the greater number of the other acids camphor is dissolved. Muriatic acid gas and fluoric acid gas dissolve it, and form a combination which is decomposed by water; and liquid muriatic acid, as well as acetic acid, easily effect its solution; and Bergius found, that water impregnated

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* Philosophical Transactions, 1803.

with carbonic acid dissolved a larger portion of it than pure water *.

By distilling nitric acid from camphor, it is more completely changed, and by this process is converted into an acid which has received the name of Camphoric acid. The process consists in distilling from 4 ounces of camphor in a retort, 1 lb. of nitric acid, so far diluted as to be of the specific gravity of 1·33, the heat being gradually applied by the medium of a sand-bath: nitric oxide and carbonic acid gases are disengaged; part of the camphor rises in vapour, while the other part receives oxygen from the acid. When the vapours have ceased, the receiver is to be unluted; the camphor condensed in it is to be returned into the retort, another pound of acid added, and the distillation is to be renewed. This operation is to be repeated, until all the camphor is acidified. According to Lagrange, who performed this experiment with care, about 5 pounds of nitric acid of the above strength are required to acidify 4 ounces of camphor †. At the end of the experiment, the camphoric acid crystallizes in the remaining liquid. The liquid is decanted off, and the crystals being placed on a filtre, are washed with distilled water, to carry off any adhering nitric acid. They amount to nearly half the weight of the camphor.

Camphor may be decomposed by heat: and the experiment is instructive, as pointing out the peculiar nature of this principle. Some management is requisite to submit it to a heat sufficiently high, and at the same time

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* Materia Medica, p. 320.

† Nicholson's Journal, 4to, vol. ii. p. 157.

prevent its volatilization. The process which has been followed, is to mix it with pure clay: six parts of clay being used to one of camphor: both are reduced to powder, and when intimately mixed, the mixture is made into a paste with water, which is made up into small balls, and well dried. These balls are exposed in a retort to a heat gradually raised, the retort being connected with a receiver containing a portion of distilled water. Part of the camphor is sublimed, but the greater part of it is decomposed; an oily fluid distils over, which swims on the surface of the water; a portion of camphoric acid is likewise produced, which the water dissolves, and there remains in the retort a quantity of charcoal mixed with the clay, and giving to the whole a deep black colour: there are disengaged too in the course of the experiment, carburetted hydrogen, and carbonic acid gases. From 4 ounces of camphor there are obtained, according to Lagrange, by this process, 12 drachms of oil, and 8 drachms of charcoal, besides the camphoric acid and aërial fluids *.

The oil of camphor, as this product of the decomposition has been named, is of a golden yellow colour; has an aromatic odour resembling that of thyme or rosemary, and an acrid burning taste, leaving, however, a sense of coolness impressed on the tongue. It is volatile: when exposed to the air it partly evaporates, and there remains a thick yellow matter, which at length also entirely evaporates. It is also volatilized by heat, and is inflammable. Alkohol dissolves it entirely, and the solution is immediately rendered milky, but without any precipitate on

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* Nicholson's Journal, 4to, vol. ii. p. 199.

the affusion of water. It combines with the pure alkalis, affording a compound soluble in water, and which has the characters of the soap made with volatile oils. When brought into contact with oxymuriatic acid, this oil becomes very white, but no precipitate appears.

This substance has evidently the properties of a volatile oil; and hence the decomposition of the camphor in which it is produced, points out the chemical constitution of this principle. As it is resolved into this oil and into charcoal, or compounds containing carbon, it is obvious, that it differs from the volatile oils principally, if not solely, in the larger quantity of carbon which enters into its composition.

It has already been stated [*], that when the vapour of camphor is transmitted through an ignited glass tube, it is resolved principally into a species of oxy-carburetted hydrogen gas, of a greater degree of specific gravity than the greater number of the gases of this family; consuming also a large quantity of oxygen in its combustion, and affording a large proportion of carbonic acid from that process: containing, therefore, evidently a large quantity of carbon in its composition.

The CAMPHORIC ACID produced by the preceding processes, has been particularly examined by Lagrange, who has found reason to conclude, that it is different from all the known acids. It has a slightly acid bitter taste, and reddens infusion of litmus. Its crystals effloresce on exposure to the air; they are sparingly soluble in cold water, an ounce of water at 50° of Fahrenheit, not dissolving more than 6 grains; at 212°, about 48 grains are dissolved. When the acid is placed on ignited fuel, it emits a dense aromatic vapour, and is entirely dissipated. By applying heat to it in close vessels, it first melts and sublimes, but by a higher heat its properties are changed; it no longer reddens litmus, acquires an aromatic smell, its taste is less penetrating, and it is no longer soluble in water, or in sulphuric or muriatic acid. Nitric acid heated on it, turns it yellow and dissolves it.

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[*] Vol. ii. p. 382.

Camphoric acid is soluble in the mineral acids: it is likewise soluble in alkohol, and in the volatile and fixed oils. It produces no change in sulphur.

The salts formed by this acid, with the alkaline, earthy, and metallic bases, are named CAMPHORATES. Their properties have been examined by Lagrange *. Their taste is somewhat bitter: they are decomposed by heat, the acid being sublimed; and they all exhibit a blue flame when heated before the blowpipe. The alkaline and earthy camphorates are formed by adding the camphoric acid to the alkali or earth, either pure, or in the state of carbonate; the carbonic acid, in the latter case, being disengaged.

Camphorate of potassa is sparingly soluble in cold, but abundantly soluble in boiling water; it crystallizes, on cooling, in crystals of six sides, white and transparent, and having a bitterish taste. It is also soluble in alkohol. It is slightly deliquescent in a humid atmosphere; is fused, and then decomposed by heat, and, as all the cam-

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* Annales de Chimie, tom. xxvii. p. 19.

phorates do, burns with a blue flame. Camphorate of soda is rather less soluble than that of potassa, either in cold or warm water: its crystals are not of a regular form; they are white and transparent, and have a bitterish taste. They are also soluble in water; they are slightly efflorescent; are decomposed by heat in the same manner as the other. Camphorate of ammonia is not easily obtained crystallized: its solution, evaporated by a very gentle heat, giving a solid matter, not transparent, which has nearly the same degree of solubility as the camphorate of potassa. It is also soluble in alkohol; is deliquescent, and decomposed by heat.

The earthy are much less soluble than the alkaline camphorates. Camphorate of lime is sparingly soluble in water, sufficiently so, however, to remain in solution when the acid is dropt into lime-water. When this solution is evaporated, the salt is deposited, on cooling, in crystalline plates, of a white colour. It is efflorescent: like the other camphorates, it is decomposed by heat. It is insoluble in alkohol. The camphorate of barytes is prepared in a similar manner; and by evaporation it is obtained, when the liquor cools, in crystalline plates. It is very sparingly soluble in water; is not altered from exposure to the air. Its taste is slightly bitter. Camphorate of magnesia is prepared by adding camphoric acid to carbonate of magnesia, diffused in water, filtrating the solution, and evaporating it: the salt is deposited in crystalline plates, white, opaque, and slightly efflorescent. Its taste is bitter: it is very sparingly soluble in water, and also in alkohol. Camphorate of argil is prepared by a process similar to that by which the last salt is obtained: on evaporation and cooling, it is deposited in the state of a white powder, having a taste somewhat bitter and styptic. It is soluble in about 200 parts of cold water, and in a much less quantity of boiling water. It is also sparingly soluble in alkohol, but more abundantly if the temperature be raised. It is decomposed by heat, and, like the other camphorates, burns with a blue flame.

CAMPHOR is not only a native production; it has been lately discovered, that it is capable of being artificially formed. This rather singular fact occurred to a Mr Kind, a German chemist, in forming a medicinal preparation, by passing muriatic acid gas through oil of turpentine. "The oil acquired at first a yellow colour, afterwards a pale brown colour, which, towards the end, turned to a deep brown. After cooling, the liquor was almost wholly coagulated into a crystalline mass, which in every respect comported itself like camphor." The agency of the muriatic acid in giving rise to this result, he supposes to depend on its great tendency to combine with water, in consequence of which it determined the union of the principles of this liquid (oxygen and hydrogen) in the oil, so that the carbon became predominant. He farther observes, that though a similar production of camphor had not been before noticed, yet Meyer speaks of a concretion of a camphoric nature, formed in oil of turpentine, digested with dry caustic salt; and Trommsdorff observed a formation of camphor, on distilling essential oils on lime; and in both these cases, the same cause may be supposed to have operated.

Trommsdorff repeated Kind's experiment, and obtained similar results. A concrete matter was procured, which, when dry, was white and semi-transparent: its odour was strong, analogous to that of camphor, though injured by that of the turpentine. When heated, it was volatilized, with a strong smell of camphor, and without leaving any residuum: in close vessels it sublimed: in the open air its vapour inflamed. It was dissolved entirely by alkohol, and was precipitated unaltered by water. It dissolved with facility in almond oil. Concentrated nitric acid effected its solution, at first calmly, but afterwards with a disengagement of nitric oxide gas. The mixture became turbid by the addition of water, but did not deposite camphor,—the only circumstance attending these experiments in which this substance differed from common camphor, and which Trommsdorff supposed might be owing to the presence of a little muriatic acid, or oil of turpentine.

These experiments were repeated by Boullay, in conjunction with Cluzel and Chomet, from whose memoir * the above account is taken; and they have added a number of other facts connected with this artificial formation of camphor.

From four pounds of oil of turpentine, put into the first bottle of Woolfe's apparatus, and submitted to the action of the quantity of muriatic acid gas transmitted through it, disengaged from four pounds of sea-salt and two pounds of sulphuric acid mixed in a retort, they obtained, at the end of the experiment, which exhibited the

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* Nicholson's Journal, vol. x. p. 132.

same phenomena as had been described by Kind, twenty ounces of a crystalline matter. When the brownish liquid which had been withdrawn from this matter had stood several days, four ounces more were deposited; and on exposing the remaining liquid to intense cold, two ounces more were obtained, thus affording, on the whole, seven ounces and a half of this matter for each pound of oil of turpentine employed. When the proportion of muriatic acid gas transmitted through the oil was increased, the precipitation of the crystalline matter took place in nearly the same quantity.

This matter, washed in distilled water, became of a beautiful white colour: it gave no signs of acidity, but had still an odour of turpentine. When washed with water having dissolved in it carbonate of potassa, it lost much of this odour. When mixed with an equal weight of charcoal powder, of quicklime, or of dry argil, and sublimed, in each of these processes, a mass was obtained in the capital, composed of needle-formed crystals in groupes. Thus purified, it had entirely lost the odour of oil of turpentine: that which it retained was analogous to that of common camphor, but not so strong. It swims on water, and communicates to it its taste: it is completely dissolved in alkohol, from which it is separated by water unaltered.

So far in its properties it is the same with natural camphor: in others, however, it is somewhat different. Nitric acid in a diluted state, which dissolved common camphor readily, had no effect on it. The concentrated acid had at first no action on it; but, after a few seconds, a solution is effected, nitric oxide gas being disengaged;

while the same acid dissolved common camphor, diffusing white vapours. Neither did acetic acid, which readily dissolves common camphor, act upon this artificial substance in the cold. On applying heat, it softened, and seemed to dissolve it; but, on cooling, it was all collected on the surface of the acid, with its properties unaltered.

When the similarity of this product in so many other properties to camphor is considered, these differences are perhaps not sufficient to invalidate the conclusion, that it may be regarded as a variety of this principle.

The French chemists found, that when oil of turpentine was kept for three days in a sand-bath, the temperature of which was about 120°, a very light and volatile oil was condensed in the receiver, and in the capital many small crystallizations of true camphor; but they conclude, that although this appears to prove, that a quantity of camphor exists in this oil, yet it could not have contained so large a quantity as that obtained by the action of muriatic acid gas on the oil; part at least, therefore, of which must have been formed during the process. They farther found, that the other volatile oils afforded no camphor when subjected to the action of the muriatic acid gas.

The liquid which is produced along with the camphor appears, from their experiments, to contain a quantity of oil soluble in alkohol and ether, and of muriatic acid.

SECT. XII.

RESIN.

THE principle to which this name is given, exists abundantly in the vegetable kingdom, and is one of those proximate principles, the characters of which are most distinct and obvious, and which has been therefore longest known. It is often in combination with some of the other principles, particularly with gum, essential oil, and extract. But there are also vegetables which exude juices that concrete into a matter entirely resinous, and it is from these that the characters of the species are taken. The essential characters are existing in the solid form, being altogether insoluble in water, but perfectly soluble in alkohol, and in essential and expressed oils; and being incapable of being volatilized without decomposition.

The resinous juices obtained, either by spontaneous exudation, or from incisions in the vegetables affording them, always contain a portion of essential oil, which, from exposure to the air, is either volatilized, or changed so as to be converted into resinous matter, or sometimes the oil is abstracted by distillation. In some plants, the concrete resin is deposited in the interstices of the wood, or other parts of the plant. When combined with gum or extract, it can only be separated by a chemical process; and the one generally followed is, to dissolve the resinous matter by alkohol, and precipitate it from this solution by the affusion of water.

Resins when concrete, are brittle, and have generally a smooth and conchoidal fracture; their lustre is peculiar, and has even been selected as affording one which is characteristic, denominated by mineralogists the Resinous: they are more or less transparent, and of a colour which is generally some shade of yellow or brown. Their specific gravity is rather greater than that of water: they are often odorous and sapid, though neither of these qualities is essential to a resin, and some are insipid and without smell.

Resins are fusible, and melt from a very moderate heat. When cooled they become solid, without any change in their properties.

They are not volatile: for although when strongly heated, a vapour arises from them, this is either from a portion of volatile oil which has adhered to the resinous matter, or is the result of decomposition. When the heat rises nearly to ignition, this vapour takes fire, and the resins themselves are all inflammable. They afford in their combustion, water, carbonic acid, and a very dense smoke which condenses into a fine charcoal. When subjected to decomposition by heat in close vessels, they afford water, a portion of acid, carburetted hydrogen and carbonic acid gases, and a residuum of charcoal. They appear therefore to be compounds of carbon, hydrogen, and oxygen; and differ from the volatile oils in containing either more oxygen or more carbon. These oils appear to be convertible into them by long exposure to the atmosphere, and it is not very evident whether this is owing to the oxygen directly combining with the principles of the oil, or to its combining with its hydrogen, forming water, and leaving the oil of course with an enlarged proportion of carbon and oxygen.

All these substances are insoluble in water, and are not affected by this fluid. Neither do they suffer any alteration from exposure to the air; hence from both qualities, they are used as the basis of varnishes, with which the surfaces of substances are covered, that require to be protected from the action of air and humidity.

Resins are soluble in alkohol; some of them, however, more sparingly than others. Those which are most difficultly soluble, have their solubility promoted by the addition of camphor. Their solutions are decomposed by the addition of water, and the resinous matter precipitated. They are soluble likewise in ether, and in volatile and expressed oils: and camphor exerts a marked action on them; when beat with any resin or gum resin, it renders it soft and nearly liquid.

From the experiments of Mr Hatchet it appears, that resins combine with the alkalis. In examining the substance known by the name of Lac *, and which consists principally of resin, with smaller portions of wax, gluten, and colouring matter, he found, that it was completely soluble in solutions of potassa and soda, forming saponaceous compounds, which are decomposed by acids, and the resin again precipitated. And by further experiments he found, that other resins are dissolved likewise by the alkalis. Facts of this kind had even been known to the older chemists: thus copal, which of all the resins seems to be least easily acted on, was known to be perfectly dis-

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* Philosophical Transactions, 1804.

solved by pure alkalis, the solution being precipitated by acids [*]. These alkaline solutions may even serve as varnishes, and in the composition of pigments. The alkaline carbonates, and even salts, having a slight excess of alkali, as common borax, exert a similar action, only less energetic. The solvent action of ammonia on the resins, is not so complete as that of the fixed alkalis.

Resins are also soluble in some of the acids, and by others are decomposed. On this subject the most accurate information is to be derived from Mr Hatchet's experiments [†]. Concentrated sulphuric acid poured on any resin in powder, dissolved it, he found, in a few minutes; the solution being transparent, of a yellowish brown colour, and an oily appearance. Though the resin appears at first to be merely dissolved, this is not permanent; progressive alterations taking place in the dissolved matter: the principal product of these changes in a certain stage of the process, is a substance which has almost all the characteristic properties of the vegetable substance known by the name of Tannin; this, however, is also changed by the continued action of the acid, and is ultimately converted into charcoal.

Nitric acid also acts on resins; but the nature of its action, it is observed by Mr Hatchet, appears to be conversely that of sulphuric acid: with the latter acid, solution precedes decomposition; but with nitric acid decomposition to a certain degree precedes solution: for it at first converts the resins into a pale orange coloured, brittle, porous substance, then into a product which apparently possesses the intermediate characters of vegetable extractive matter and of resin; and, lastly, into a variety of the tanning substance; different proportions of this being afforded by different resins.

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[*] Materia Medica Bergii, p. 899.

[†] Philosophical Transactions, 1804, 1805, 1806.

There is one acid, however, which appears to be a direct solvent of resins, without materially altering their composition,—the acetic acid. Mr Hatchet observed its solvent power, in his analysis of lac; the whole of the resin of that substance being dissolved by it, with the assistance of heat, a portion being deposited as the liquid cooled, but a part still remaining dissolved, which was afterwards precipitated by water.

A number of resinous substances are met with in commerce, being used in medicine or the arts; such as copal, sandarach, mastic, dragon's blood, elemi, and the resins obtained from the juices of the different species of pine. These, though a general analogy exists among them, still differ somewhat in their chemical properties, so as to lead them to be regarded as varieties of one chemical species. They hence require some separate notice.

The juice of the Pinus larix, balsamea, sylvestris, and abies, consists principally of essential oil and resin. The oil when separated by distillation, which it is usually from the Pinus larix, is known by the name of Oil of Turpentine, and the substance which remains is the common resin, or rosin of the shops. It is of a white or yellow colour, and has hence the names of *Resina flava*, and *Resina alba.* Its properties are those of a pure resin, above described.

Sandarach is the produce of the Juniperus communis, being secreted and deposited beneath the bark, or exuding through it. It is in small round fragments, of a yellowish colour, semi-transparent, and brittle, having a very slight odour, and scarcely any taste. It is entirely soluble in alkohol, and is used in the composition of some of the spirit varnishes. Mr Nicholson remarks, that it is not soluble in oil or melted tallow, in which it differs from resins *.

Mastich is the produce of the Pistacia lentiscus, by exudation: it is in small rounded masses, of a yellowish colour, semi-transparent: it has scarcely any taste, and its smell is perceptible only when it is heated. It is soluble in alkohol, but not entirely. Mr Mathews found, that nearly a fifth part of it remained undissolved: this residual matter, after repeated washings with alkohol, was white, considerably elastic, adhesive, and inflammable. It had much the appearance of caoutchouc, and, from some comparative experiments, it appeared to have very nearly the same chemical properties. Mr Brande has remarked, that it differs from it, in becoming hard when dried, by exposure to the air.

Copal is a resin possessed of some peculiar properties, and valuable, as serving to form the finest varnishes. It is the produce of the Rhus copallinum, a native of Mexico: it appears to have exuded from the stem or branches in a liquid or soft state, and to have afterwards become concrete. It is in large fragments, smooth and brittle, transparent, or nearly so, without colour, or having only a slight tinge of yellow: its taste is weak, and it has scarcely any smell: when chewed, it does not become tough, as mastich does. Like the other resins, it is fusi-

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* Nicholson's Journal, vol. x. p. 247.

ble, inflammable, and altogether insoluble in water. The property in which it differs from the greater number of them is its very sparing solubility in alkohol: when digested in that fluid, with the assistance of heat, part of it assumes the appearance of an opaque, soft, viscous mass; a small portion only is dissolved, and the greater part of this subsides as the liquid cools. Camphorated alkohol, Bergius states, dissolves the greater part of it; and a perfect solution is obtained, he remarks, when camphor and copal are put together into alkohol, owing, no doubt, to the peculiar action which camphor exerts on all the resins. It is not soluble by digestion in expressed oils; but it is stated by Bergius, that if it be previously melted, and the oil be dropt on it, it is completely dissolved both by fixed and volatile oils. By oil of turpentine, he adds, it is converted into a soft viscid-like substance; but if the oil be old, it acts more powerfully on the copal than when recent. Other oils, as those of rosemary and lavender, dissolve it even in the cold. And as these three oils, especially when long kept, appear generally to contain camphor, it is probable that it may promote the solution of the copal.

Elemi is a resin very little used. It is the produce of the Amyris elemifera; is in large solid masses, of a variegated greenish colour, and semi-transparent; having an odour stronger than some of the other resins, and a taste which is bitter. It is fusible, inflammable, and soluble in alkohol, and partially in expressed and essential oils. It appears usually to contain a portion of volatile oil in combination with resin, as a small quantity is obtained from it by distillation.

Animi, the produce of the Hymenæa courbaril, is a resin which, in its external appearance, has a very strong resemblance to copal, and is often sold for it, or mixed with the real copal; it is distinguished principally by having more of a yellow tinge, by becoming somewhat ductile when masticated, and by being more easily soluble in alkohol, and in essential or expressed oils.

The resin, which has received the absurd name of Dragon's Blood, is obtained from the Pterocarpus draco, exuding from incisions made in the bark, and also from some other plants. It is in masses, of a red colour, and variegated texture, opaque, hard, and friable; without taste or smell. It is fusible, inflammable, and soluble in alkohol, communicating to it a deep red colour.

The substance known by the name of Lac is produced by an insect, which deposites it on the branches of certain trees in India, formed into cells, which appear designed as an envelope for its young. It is imported into Europe in different states,—stick lac, which is the substance in its natural state; seed lac, in which it is reduced into small fragments or grains by pounding, and from which part of the colouring matter appears to have been extracted by boiling; and shell lac, which is prepared from the natural lac, by liquefying, straining, and forming it into thin plates, and which contains least of the colouring matter. The lac, freed from the insect often involved in it, has all the characters of vegetable matter, and is probably not formed, but deposited by the animal which produces it; and Mr Kerr, who has given some account of its natural history *, has remarked, that " as a red substance is ob-

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* Philosophical Transactions, 1781, p. 229.

tained by incision from the plaso-tree very analogous to lac, it is probable, that the insects have little trouble in animalizing the sap of these trees in the formation of their cells." It was always evident, from the chemical nature of this substance, that it was of a resinous nature; and its analysis has lately been executed by Mr Hatchet *. He has found it to consist principally of resin, with colouring extract, vegetable gluten, and wax; the different varieties giving the following proportions:

	Resin.	Extract.	Wax.	Gluten
Stick lac,	68	10	6	5.5
Seed lac,	88.5	2.5	4.5	2
Shell lac,	90.9	0.5	4	2.8

The principal qualities of the lac are of course derived from the resin, its chief constituent part. Alkohol dissolves this, forming in the cold a transparent solution; but if heated, the solution is turbid, from some of the other principles being dissolved. Ether acts less powerfully on it. Water acquires from the different varieties of lac a crimson colour, more or less deep, according to the proportion of colouring matter they contain. The stronger acids, as the sulphuric and nitric, decompose it. Muriatic acid dissolves its colouring matter, and gluten; acetic acid dissolves the whole of it, except the wax. The alkalis and alkaline carbonates dissolve it, forming saponaceous solutions; and it is also rendered soluble by borax. Lac is used in dyeing, and the preparation of paints;

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* Philosophical Transactions 1804.

a solution of it in water, by the medium of borax, is the basis of the Hindoo ink, and may be used as a varnish. It enters into the composition of the common spirit varnishes, and is employed also in the formation of sealing wax.

Besides the substances now described, which are nearly or perfectly pure resins, resinous matter exists in combination with other proximate principles of vegetables, and is also contained in the leaves, bark, and other parts of many plants. The medicinal powers of a number of the most important articles of the Materia Medica depends on a resinous principle in these states.

The principal use of the resins, it has been observed in their description, is in the formation of varnishes; and these are generally composed of more than one resin in a state of solution. They are named Oil or Spirit Varnishes, according as oil or spirit is the solvent. The oil may be either expressed or volatile. Of the former, the drying lintseed oil is what is generally employed; of the latter, oil of turpentine. A varnish with the first is prepared by boiling the finer kind of common resin with a portion of mastich in lintseed oil; and to this a portion of oil of turpentine is usually added, which accelerates the drying of the varnish. Varnish with oil of turpentine alone is prepared by dissolving in this oil the requisite proportion of mastich. If a finer varnish of this kind is required, it is formed from copal; but it has always been found difficult to dissolve the copal completely in the oil. Different methods have been proposed; that by the medium of camphor, which, as has already been remarked, renders copal soluble, appears to be the best. This varnish is colourless and durable, and answers well for varnishing pictures. The method of preparing it has been given by Mr Sheldrake *: half an ounce of camphor being dissolved in a quart of oil of turpentine, and a piece of copal the size of a large walnut being reduced to coarse powder, and put into it, in a tin bottle capable of holding two quarts, having a long neck, with a cork fitted to the mouth, in which there is a notch or small hole to allow of the escape of the vapour when the oil is volatilized by heat. The heat is applied so as to make the oil boil quickly, and it is kept boiling gently for about an hour, when so much of the copal will be dissolved as to form a proper varnish. Mr Sheldrake likewise found, that copal might be dissolved in oil of turpentine by the medium of ammonia †; but he prefers the copal. Spirit varnishes are prepared from resins dissolved in alkohol. Those usually employed are mastich, sandarach, lac, and copal; and some of these are frequently mixed. A colourless varnish is obtained, by dissolving mastich or sandarach either alone or mixed in alkohol; a portion of turpentine being often added, to render the varnish less brittle. The solution of copal, however, is preferable, as being perfectly colourless: but there is with regard to it the same difficulty of dissolving it in alkohol as in essential oils; and to promote its solution, camphor is in this case also the best medium. The recipe for this varnish has been thus given by Mr Sheldrake: "Dissolve half an ounce of camphor in a pint of alkohol; put it in a circulating glass, and

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* Nicholson's Journal, 8vo, vol. ix. p. 157.

† Ibid. p. 154.

add four ounces of copal in small pieces; set it in a sand heat, so regulated, that the bubbles may be counted as they rise from the bottom; and continue the same heat till the solution is completed *." Lac forms a varnish which is always coloured, and is hence used only in those cases where the colour is of no importance, or is even of advantage, as in lackering brass, or in laying on a coloured ground. The following recipe has been given for a varnish for this purpose: " Dissolve two ounces of very pure and fine gum-lac in 48 ounces of alkohol, and place the solution in a sand-bath exposed to a moderate heat. To prevent the too abundant evaporation of the spirit of wine, as well as the bursting of the glass, a piece of bladder ought to be bound over the latter, and a few holes made in it with a needle. In another glass dissolve, in the same quantity of spirit of wine, an ounce of dragon's blood in grains. When both the solutions are completed, mix them together; then put three grains of yellow wood into it, and suffer it to remain there twelve hours in a moderate heat: after which, strain the liquor through filtering paper †."

From the combination of lac with what is named Venice Turpentine, sealing wax is formed. Four parts of lac are said to be melted with two of turpentine, and two of resin; and the composition is coloured red by the addition of one part of cinnabar and one of red lead, or black, by the addition of lamp-black.

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* Nicholson's Journal, 4to, vol. iii. p. 447.

† Philosophical Magazine, vol. xi. p. 148.

THERE exists in many vegetables, a natural and intimate combination of resin with gum, forming what has been named GUM RESIN, and which some have classed as a distinct proximate principle. The proximate principles of vegetables, however, are those substances formed immediately from the combination of the ultimate elements; they are specific and determinate in their composition; and native mixtures, or combinations of them with each other, cannot be placed as distinct principles, though such substances may be entitled to some notice, as articles of natural history, or as of importance in medicine or the arts.

A number of medicinal substances are gum resins,—such are aloes, ammonia, assafœtida, euphorbium, galbanum, gamboge, myrrh, sagapenum, and scammony. They are all solid, generally brittle and opaque; they have frequently a strong smell, and a pungent or bitter taste. They appear to consist of various proportions of resin and gum; the gummy matter predominating in some, as in aloes; the resinous in others, as in myrrh. Their properties are derived from those of the two immediate principles of which they consist. Thus they are only partially soluble in alkohol or in water; the former dissolving principally the resin, the latter principally the gum: but in each case, part of the one principle appears also to be dissolved by the medium of the other; probably in consequence of their mutual affinity. They are almost all entirely soluble in diluted alkohol, consisting of equal parts of alkohol and water; and many of the tinctures of the shops, are solutions of this kind. By trituration with water, they generally form milky mixtures; the resin being suspended by the medium of the gum: and on standing, a great part of the resin is deposited. According to Hatchet's experiments, these substances, at least those of them which he tried, are soluble in alkaline liquors: the changes they suffer from the acids, are not precisely the same as the resins; they are decomposed, but they appear to be less susceptible of affording artificial tanin; a number of them not affording it from the action either of sulphuric or nitric acid, and others giving only small quantities. This is probably owing to the predominance of gum, or of a matter analogous to it, in their composition; as this principle appears from Hatchet's experiments, to be less easily convertible into tanin than resin is: it affords rather oxalic acid: and Fourcroy has remarked, that this acid is produced by the action of nitric acid on gum resins.

The gum resins are not fusible, but when heated soften, and, if the heat is raised sufficiently high, are decomposed. It has been observed, that in destructive distillation they afford ammonia, with the usual products of vegetable matter.

The consideration of the different gum resins, belongs rather to materia medica or pharmacy, than to chemistry. The medicinal powers of many vegetables, appear to depend on such combinations.

GUAIAC, a substance obtained by spontaneous exudation from the Guaiacum officinale, has been usually considered as a gum resin, containing a large proportion of resin. From Mr Brande's experiments *, however, it appears to possess

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* Philosophical Transactions, 1806.

some chemical properties, indicating a peculiarity of composition, different from that either of resin, gum resin, or any of the analogous vegetable principles.

Guaiac is concrete, brittle, and resinous in its appearance; it is of a grey colour, but has externally a greenish colour; this it assumes from the action of the air: for its powder, which is at first grey, gradually becomes greenish, from exposure: it also assumes the same colour when confined in oxygen gas: and this property of changing its colour, is one character which discriminates it from the resins. When digested in distilled water with a moderate heat, a small portion is dissolved, which, from Mr Brande's experiments, appears to be extractive matter, with a little lime. Alkohol dissolves it with facility, leaving a little foreign matter, not exceeding 5 parts in 100, undissolved. This solution is rendered milky by water; and it is decomposed by different acids, with phenomena that are peculiar. Muriatic acid throws down an ash coloured precipitate: Liquid oxymuriatic acid, one of a very beautiful pale blue. Sulphuric acid, when not added in too large a quantity, separates the resin of a pale green colour. Nitric acid, diluted with one-fourth its weight of water, causes no precipitate until after some hours. The liquid at first assumes a green colour, and if water be added, a green precipitate may be obtained: the green colour soon changes to blue, when, by the same means, a blue precipitate may be obtained: it then becomes brown, and a brown precipitate spontaneously makes its appearance. Acetic acid does not form any precipitate: and it has already been observed, that this acid is generally a solvent of resinous matter.

The changes of colour in the solution of guaiac in alkohol, by nitric and oxymuriatic acids, are peculiar to it, and are highly distinctive; they appear to be connected with changes of oxygenizement, to which this principle seems liable, and which are marked in it by change of colour.

The acids in-directly acting on guaiac, likewise exhibit some peculiar phenomena. Muriatic acid dissolves a small portion, the solution assuming a deep brown colour: but if heat be applied, the resin melts, and this prevents its further solution. Sulphuric acid forms with it a deep red liquid, which, when fresh prepared, deposites a lilac coloured precipitate on the addition of water: if heat be applied, the resin is decomposed and charred. Nitric acid exerts a more powerful action on guaiac, than on any of the resins; even in the cold the powder assumes a dark green colour: there is a violent effervescence from the emission of nitric oxide gas, and the whole is dissolved. This solution, when recent, gives a brown precipitate with the alkalis: after it has stood for some hours undisturbed, it deposites a considerable proportion of oxalic acid. When the guaiac is treated with diluted nitric acid, the results are somewhat different; a slight effervescence takes place, part of the resin is dissolved, and the remainder is converted into a brown substance, resembling the precipitate from the solution in alkohol. This brown substance, Mr Brande supposes, is guaiac altered by oxygen, being the last result of the oxygenizement of the guaiac. It possesses the properties of resin in greater perfection than the original, is soluble in alkohol, and also in ether, which guaiac is very sparingly; it is also insoluble in water. If fresh portions of nitric acid be added to it three or four times successively, it loses these properties; becomes equally soluble in water and alkohol, and acquires an astringent bitter taste, forming probably one of the varieties of artificial tannin.

Guaiac is soluble in the pure alkalis, and in the alkaline carbonates, forming greenish brown liquids. From the solvent powers which they thus exert on it, they do not precipitate it from its solution in alkohol.

Subjected to destructive distillation, it gave an acidulated water, a thick brown oil, a thin empyreumatic oil; charcoal remaining in the retort, and gases consisting chiefly of carbonic acid and carburetted hydrogen being extricated. The charcoal amounted to 30.5 grains from 100, and yielded, on incineration, 3 grains of lime.

It follows, from this account of the properties of guaiac, that although it possesses many properties in common with resinous bodies, it differs from them in others: particularly in affording extractive matter; in the singular alterations which it suffers when subjected to the action of bodies which readily communicate oxygen; in being capable, by oxygenizement, of being converted into a more perfect resin; in yielding oxalic acid, when treated by nitric acid; and, in the large quantity of charcoal and lime which it yields on destructive distillation,—differences which, as the chemist who has investigated these properties remarks, probably arise from certain peculiarities in the proportions and chemical combination of its constituent elementary principles.

THE substances which have been named **BALSAMS**, consist principally of resin, with which are united a quantity of the peculiar vegetable acid named Benzoic, and in some of them a portion of essential oil. The same remark applies to them as to the gum resins,—that they cannot properly be regarded as constituting a distinct proximate principle of vegetables, since they are simply a mixture or combination of other known principles. Some chemists indeed have supposed, that the benzoic acid which they afford, is not previously contained in them, but is actually formed in the process by which it is extracted. This opinion was advanced by Gren, and appears to be also adopted by Mr Hatchet, from his experiments on its production, when the balsams were acted on by sulphuric acid. But the various processes by which it is procured, are unfavourable to this opinion. It is separated from the balsams by the application of heat, by boiling them with water, or with alkaline solutions, or digesting them with acids; and it is not very probable, that agents so very different in their chemical actions, should, in this particular instance, give rise to the formation of precisely the same product. The action of some of them too, appears not sufficiently energetic, to be capable of producing such an effect. The heat that requires to be applied to volatilize the acid from the balsams, is extremely moderate; and we have no example in which water, by any affinity it exerts, *causes* the formation of a new principle. It appears therefore more probable, from these considerations, that this acid pre-exists in the balsams, and that it is extracted, not formed, by the processes by which it is obtained: that of course they do not constitute an immediate principle of vegetable matter, but are combinations of others.

Their chemical properties are derived from the principles of which they consist: when exposed to heat, they melt like the resins, and at the same time they exhale a fragrant and acrid vapour, which is the benzoic acid, and which may be easily condensed in needle-like crystals. If heated more strongly, a portion of oily matter is volatilized: subjected to destructive distillation, they afford, besides benzoic acid, products similar to those from the resins: when heated in the open air, they inflame.

They are insoluble in water; but by digestion with it, a portion of benzoic acid is dissolved, which, as was long ago discovered by Geoffroy, may be obtained, by evaporation and cooling, crystallized. According to Fourcroy, their powder, when merely mixed with the vegetable colours diffused in water, reddens them,—a proof of the presence of free acid. When distilled with water, a small quantity of essential oil is obtained from the greater number of them.

They are perfectly soluble in alkohol, any impurities excepted; and the solution is decomposed by the affusion of water, the resinous matter being precipitated. It is also decomposed by some of the acids. They are likewise soluble in ether, and in the volatile oils, and are softened by the action of camphor.

The action of the alkalis on the balsams, is similar to their action on the resins,—dissolving them and forming brown solutions. The alkali at the same time combines with the benzoic acid; and if the solution has been dilute, so as to prevent the solution of the resinous matter, the filtrated liquid has not much colour, and on saturating the alkali with an acid, benzoic acid is obtained. The action of lime, by the medium of water, is similar.

The stronger acids, particularly the sulphuric and nitric acids, when digested on the balsams, caused, in Mr Hatchet's experiments, a formation of tannin, in the same manner as the same acids do from the resins. There was also, in some cases, a formation of prussic acid; and benzoic acid was always obtained by sublimation or distillation from the mixture. This acid, it will afterwards appear, is not decomposed by sulphuric or nitric acids; and hence its appearance in this process, supposing it to pre-exist in the balsams. Acetic acid when heated, dissolves some of the balsams, as benzoin, as Mr Brande found, in his experiments on this substance *: it retains the resin in solution, but as it cools, allows the benzoic acid to precipitate.

All the balsams are odorous, and pungent. Some of them, as benzoin, are solid; others are fluid, but thick; and these by age likewise become solid: they exude from the vegetables which produce them, either spontaneously or from incisions made in the bark. The principal substances of this class, are Opobalsam, or Balsam of Gilead, the produce of the Amyris Gileadensis; Balsam of Peru, from the Myroxolon Peruiferum; Balsam of Tolu, from the Toluifera Balsamum; Benzoin, from the Styrax benzoinum; and Storax, from the Styrax officinale. They are used sometimes in the practice of medicine, and their

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* Nicholson's Journal, vol. x. p. 8

individual history belongs to the materia medica. Their chemical properties are very nearly the same.

SECT. XIII.

EXTRACT, OR EXTRACTIVE MATTER.

THE name of Extract has, in the language of pharmacy, been appropriated to a preparation in which vegetable juices, or the watery decoctions of vegetable substances, are reduced by evaporation to a thick consistence. From the nature of this process, it is evident, that the product may consist of different principles, of gum, sugar, tannin, saline matter, and indeed of all those soluble in water, and that, as obtained from different plants, it may be very different. Preparations of this kind being much used in the medical practice of France, have always engaged the attention of the French chemists, and they were accustomed to arrange them under certain divisions. Thus, Rouelle distinguished three principal kinds; what he named Mucilaginous extracts, soluble in water, in which gum, or mucilage predominates; Resinous extracts, in which the properties denote the presence of resin, and which are hence more especially soluble in alkohol; and Saponaceous extracts, which are soluble both in water and alkohol. A different view, however, has been since taken of this subject: it has been conceived, that though in these preparations there may be an intermixture of different principles, yet there is one which forms their basis, and which constitutes a peculiar vegetable principle, distinct from any other. It is to denote this, that the name Extract, or Extractive Matter is now applied.

This view of the nature of this principle, has been principally given by Fourcroy and Vauquelin, in the course of their analysis of different vegetables: by the former particularly, in his analysis of the cinchona of St Domingo*, and by the latter, in his analysis of the sap of the elm, beech, chesnut, and other trees †; and it is from their researches, that the history of this principle is chiefly to be derived. Hermbstaedt has also stated some facts with regard to it. There is still, however, as I shall have to remark in concluding its history, a considerable degree of obscurity and doubt as to the nature of this matter; whether it can properly be regarded as a well-defined proximate principle, uniform in its composition and properties; or whether it may not be a mixture or combination of some of the other known principles of plants. The term Extract, which has been applied to it considering it as a distinct principle, is ambiguous, from the other signification which has been attached to it, and under which, in the language of pharmacy, it is still understood. Were the existence of this principle fully established, the name of Extractin might perhaps be given to it, and would be free from all ambiguity.

Extractive matter, according to Fourcroy, exists in different parts of plants, but more particularly in the green and brown solid parts, as in the leaves, bark, and wood:

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* Annales de Chimie, tom. viii. & ix.

† Ibid. tom. xxxi.

it is also often naturally dissolved in their juices. When it exists in the solid parts, it is best obtained by boiling the solid matter repeatedly in water, and evaporating the strained decoction: when dissolved in the juice, it is obtained by evaporating this to a solid form, by a gentle heat. In either case, however, it is obvious, that it may, and indeed generally will be, mixed with other principles: there is no process by which these can be separated, so that we are certain of obtaining it pure: and hence its properties are rather discovered, either from examining it as afforded by some vegetables with little intermixture, or from the effects re-agents produce upon the juices or decoctions containing it, and which cannot be supposed to arise from the operation of these on other known principles.

Extractive matter is soluble in water, but it gradually becomes insoluble from exposure to the air. According to Vauquelin, the juices which naturally contain it, are colourless as they issue from the plant, but they soon assume a yellow or brown colour, from the action of the air and light. If evaporated, a brown or reddish pellicle forms on their surface, which breaks and subsides, the dissolved matter becoming insoluble; and when the whole is reduced by evaporation to a thick consistence, on attempting to dissolve this in water, a portion always remains undissolved. Fourcroy has observed too, that if the decoction of a vegetable which affords extract, be filtered, so as to be perfectly transparent, by merely continuing the decoction, it becomes turbid, and a great part of it is precipitated from the water, in a state in which it is no longer soluble: the longer the boiling is continued, and the more freely the liquor is exposed to the air, the more insoluble matter, he adds, is formed; and by continuing the successive solutions and evaporations, the whole of the soluble extract may at length be brought into this state.

This change he ascribes to the absorption of oxygen: and this is one principal property characteristic of this principle,—that it is soluble in water, but when in solution, and at a high temperature, it absorbs oxygen and becomes insoluble, and at the same time comparatively insipid and inert. The injury which many medicinal plants sustain from boiling, has been ascribed by Fourcroy to this cause, and not to the dissipation of any active volatile principle, as had formerly been supposed; and indeed from many of them which are injured by this operation, no such principle can be obtained, when the operation is performed, so as to collect the products.

Theodore Saussure has observed, that Fourcroy, in ascribing these changes to oxygenizement, does not affirm that he had submitted the insoluble matter to analysis, or the air, in contact with which the liquid had been boiled, to any eudiometric trial. He therefore placed, under bottles full of atmospheric air, and closed by quicksilver, capsules containing solutions of the extractive matter of cinchona, oak wood, and different moulds: after some days, he found precipitates had formed in these solutions, and the air had, at the same time, suffered a small diminution of volume. Submitted to eudiometric examination, it was found to have lost its oxygen, which was replaced by a quantity of carbonic acid gas, not equal in volume to the oxygen that had been consumed part of this acid having been absorbed by the water of the solutions; hence, when previously saturated with carbonic acid gas, the quantity of carbonic acid formed under their exposure to atmospheric air, was exactly equal to the quantity of oxygen that disappeared. He further found reason to conclude, that in thus losing part of their carbon, by the action of oxygen, they lose still more of their oxygen and hydrogen, by these principles entering into binary combinations and forming water, and that hence the residual insoluble matter has an enlarged proportion of carbon, and is not merely, as Fourcroy had inferred, extract oxygenized*.

Extractive matter is soluble in alkohol, as is evident from its being abstracted by this fluid from vegetable matter, in which it exists; and this solution is not decomposed by the affusion of water. This property of equal solubility in water and in alhohol is very well shown in some vegetables, as, for example, in saffron, which yields a large portion of matter to both these fluids, the solution in either not being altered by the addition of the other. This may therefore be regarded as another characteristic property of extract, and as serving very well to distinguish it from gum, resin, or any mixture or combination of these; gum being soluble in water, and not in alkohol,—resin in alkohol, not in water. Gum resin is indeed partly soluble in either of these fluids, but it never is entirely so; since, if it contain so much gum as to be soluble in water, it is very partially dissolved by alkohol; or, if it contain so much resin as to be soluble in alkohol, it is then imperfectly dissolved by water. And if a gum resin be digested either with water or alkohol alone, the solution it affords with the one fluid is decomposed by the other.

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* Recherches sur la Vegetation, p. 136

According to some chemsits, extractive matter is insoluble in ether. This, if the observation be just, would afford a very characteristic property of this principle. I have found, however, that sulphuric ether dissolves very readily the colouring matter of saffron, which Hermbstaedt gives as an example of pure extract, and which appears to be so.

Oxymuriatic acid, poured into a solution of extractive matter, converts it immediately into a concrete substance of a deep yellow colour, insoluble in water, but soluble in alkohol, and in the alkalis *. If cloth be steeped in oxymuriatic acid, and then immersed in a solution of extract, the oxygen is transferred from the acid to the extract, which is then deposited on the cloth, and adheres to the vegetable fibre. It was by the action of oxymuriatic acid, that Vauquelin precipitated the extractive matter from the vegetable juices which he examined.

This principle has an attraction to argil, and to metallic oxides, as appears from Vauquelin's experiments. If to a solution of it in water there be added a solution of alum, of which the excess of acid has been previously saturated, on boiling them for a short time, an abundant flocculent precipitate is formed, composed of the extract in combination with the argil of the alum; and the solution at the same time is nearly deprived of its colour. If cotton or

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* Fourcroy. Annales de Chimie. tom. vi. p. 180.

thread impregnated with a solution of alum, be macerated in a solution of extract, and boiled in it, the vegetable fibre becomes tinged of a yellowish brown colour, from the extractive matter being fixed in it by the medium of the alum; and in this way the solution may at length be deprived of nearly all its dissolved matter, and the cloth dyed. Many of the metallic salts have a similar effect. The solution of muriate of tin, in particular, forms in the solution of extract a very abundant flaky precipitate, of a brown colour, consisting of this principle, more or less oxygenized, in combination with the oxide of tin.

Extractive matter, in a humid state, gradually suffers decomposition. When its watery solution is kept for some time, it becomes turbid, deposites abundant mucous flakes, becomes mouldy at the surface, yields ammonia, and, when the putrefaction is complete, leaves, as the fixed products, carbonates of potassa and lime.

When subjected to destructive distillation, it affords an acid in part saturated with ammonia.

Such are the characters assigned to this principle; the most distinctive of which are, its equal solubility in water and alkohol; its great susceptibility of oxygenizement, and forming, when it has undergone that change, an insoluble matter, approaching to the nature of resin; and its affinity for argil and metallic oxides. It is afforded by many vegetables, and in very different quantities, and perhaps also of variable purity. Saffron has been given as an example of a vegetable matter containing a large proportion of it, and that nearly pure; 16 ounces of it affording, it is stated, 10 ounces of extract, the remaining parts being principally ligneous fibre. Other medicinal plants *contain it, and the efficacy of many of their infusions and tinctures has been supposed to depend on it.* Valerian is said to afford it in as large a quantity as saffron. It exists in gentian, senna, ipecacuan, and a number of leaves and roots. Opium and Peruvian bark contain a principle which so far has the characters of extract, that it is precipitated and rendered inert when boiled in water, with the contact of the air. It is contained also very generally in the juices of plants, obtained either from incisions of the growing plant, or from expression of their succulent parts.

I must observe, however, that the characters of this principle, as obtained from different vegetables, are by no means uniform, and that sometimes it approaches in its properties to other known principles. Thus, the active matter of Peruvian bark has one of the characters of extract, that of absorbing oxygen when in a humid state, or when boiled in water. But at the same time it approaches in other characters to a resin, as it is more soluble in alkohol than in water. The case is the same with the extractive matter of opium, while, in other vegetables, the reverse sometimes obtains; thus, the extractive matter of gentian appears to be more soluble in water than in alkohol.

Nor are the characters which have been assigned to this principle so distinctive, but that perhaps they may be presented by other vegetable principles in certain states of mixture or combination; and it is in such states that it has usually been obtained. Thus, in the juices of plants submitted to examination by Vauquelin, and in which the extractive principle is supposed to be contained, he always *found considerable proportions of saline matter, particularly of free acetic acid, and of the acetites of potassa and* lime. These might so far modify the principles existing in the juices, as to disguise their properties; acetic acid, for example, would render a portion of resinous matter soluble in water. Hence the peculiar properties which the vegetable matter in these juices did present might arise from these modifications, and not from the presence of any peculiar principle to which they belonged. From this, the solubility in water of principles otherwise not soluble might originate; and the properties of absorbing oxygen, or exerting affinities to certain earths or metallic oxides, are in some measure possessed by various vegetable proximate principles; they may be exerted more readily by them in such a state of intermixture, and can scarcely, therefore, be regarded as distinctive of extract.

From these considerations, there appears some reason to doubt of the existence, as a distinct proximate principle, of the matter to which the name of extract has been given.

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[*] The Extracts which are prepared in pharmacy, either by inspissating expressed vegetable juices, or boiling vegetable matter in water, and evaporating the decoction to a thick consistence, are very various in their composition. Those prepared by the latter process may contain mucilage, saccharine matter, tannin, and a portion of resin. The inspissated juices, besides these, may also be in part composed of the vegetable acids, and of other saline matters;

and, from analysis, they appear always to contain acetites of potassa, lime, and ammonia, often free acetic acid, and sometimes sulphate and muriate of potassa, and sulphate of lime. They usually redden infusion of litmus, exhale vapours of acetic acid, when acted on by sulphuric acid, and give a smell of ammonia when mixed with lime. As obtained from different plants, these preparations must no doubt vary in their composition. They appear also to be very liable to decomposition on keeping, and the powers of the substances from which they are prepared are often injured by the decoction or inspissation: hence they are now little used in medical practice.

SECT. XIV.

TANNIN.

A NUMBER of vegetable substances, some of them inspissated exuded juices, others barks, or leaves, had received the name of Astringents, as possessed of the common property of astringency, characterized by the power of corrugating the animal fibre. They had been, from this property, employed in medicine; and the more powerful of them were used in the operation of tanning. From some chemical phenomena which they exhibit, it appeared, that they contain a common principle to which this quality is owing; since, even where it exists in a very slight degree, it is capable of being discovered by chemical tests. If to the watery or spirituous infusion of any of these vegetable astringents, a few drops of the solution of the sulphate, or any of the other salts of iron, be added, a colour is produced more or less deep, of a blue or purple tinge, approaching sometimes to black. In those vegetables which have no astringency, no such effect is produced, while, in those possessed of this property, the deepness of the colour is in some measure proportioned to the degree in which it belongs to them.

It appeared to follow, from these facts, that the property of astringency in vegetables must depend on a distinct principle, contained in greater or less quantity in the different astringents. The investigation of this accordingly engaged the attention of chemists. The Dijon Academicians observed, that the astringent principle appeared to have some of the properties of an acid: And at length Scheele discovered, that an acid of a peculiar nature existed in the excrescence which forms on the branches of the oak, known by the name of the Gall Nut, which is one of the most powerful of the vegetable astringents, and might be obtained from it perfectly pure. This acid, named the Gallic, from the substance from which it is extracted, has the property of giving a purple colour to the salts of iron: it exists in all the powerful astringents; and being thus apparently connected intimately with the property of astringency, it was regarded as the astringent principle.

To this conclusion, however, Berthollet many years ago stated some very valid objections. He observed, that a solution of the gallic acid, reduced to as great a degree of purity as possible, added to a solution of sulphate of iron, does not produce any black colour or precipitate immediately, but only by degrees, and after some hours; while a small quantity of the infusion of galls instantly produces a much more intense colour, and greater opacity. He farther found, that by two successive decoctions of galls in water, the acid is extracted from them, so that the liquors obtained by a third or fourth decoction do not redden litmus paper, nor afford any gallic acid by evaporation, and yet they still precipitate iron copiously from its solutions. There were even some kinds of galls, those of a white colour, as well as some other strong astringents, as sumach, or walnut-tree bark, which contained no sensible quantity of gallic acid; yet these readily produce the black colour. And, lastly, the pure gallic acid has no sensible corrugating power, and scarcely any even of the peculiar astringent or styptic taste, but is merely sour *.

These facts appeared to lead to the conclusion, that although the gallic acid might be contained in the vegetable astringents, it could not be considered as the principle of astringency, but that this property must depend on some other principle, or on some modification of composition.

Deyeux, in his analysis of the gall nut †, found, that, besides the gallic acid, it contained a portion of extractive matter, and of what he considered as a particular kind of resin, or substance approaching at least to resin in some of its properties; that these are in a state of combination so as to be always extracted, either by water or alkohol;

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* Elements of the Art of Dyeing, vol. i. p. 90, &c.

† Annales de Chimie, tom. xvii. p. 1.

and the astringent property he conceived arises from this combination, and not from any of these principles alone.

At length Seguin, in the course of some experiments on the art of tanning *, established more clearly the existence of a principle in the vegetable astringents, different from the gallic acid, and on which the astringent or corrugating quality seems more peculiarly to depend. From being the agent that is peculiarly concerned in the process of tanning, it has received the name of Tan, or Tannin : and its properties are unquestionably sufficiently appropriate to characterize it as a distinct principle. Proust, Davy, and Hatchet, have by their researches extended our knowledge of its chemical relations : the two first have principally investigated its properties, and the last chemist has, by a very extensive series of experiments, established the singular fact of its artificial formation.

This principle does not appear to be secreted pure by vegetables, or deposited in any of their parts in an insulated state. It requires to be extracted by certain processes, and, as obtained by these, is frequently mixed or combined with other principles. It is contained in large proportion in the gall nut and in oak bark, sumach, and several other barks ; and the inspissated juice of the Mimosa catechu, the catechu or *terra japonica* of the shops, consists principally of it in combination with extractive matter.

If oak bark be macerated in water, the tannin and the gallic acid which are combined in it with the ligneous fibre, are dissolved, forming a liquor of a dark brown colour and a bitter acerb taste. If to this solution, freed by filtration from any undissolved matter, a solution of the animal principle, denominated Gelatin, of which isinglass or glue are examples, be added, a thick flocculent precipitate or magma is formed, which subsides to the bottom; the liquor above contains the gallic acid, and any mucilage or extractive matter which may have been dissolved from the bark. A similar appearance results from the infusion of galls treated in the same manner.

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* Annales de Chimie, tom. xx. p. 38.

This is the original experiment of Seguin, by which he demonstrated the existence of a principle in the infusions of these astringents, the characteristic property of which is, forming with animal gelatin an insoluble compound, and in consequence of which property it can be withdrawn from other principles with which it is combined.

It is obvious, however, that by such a process we do not obtain this principle pure, and that some additional steps are requisite to separate it from the gelatin with which it has combined; or that some other method must be followed to obtain it in an insulated state. Different processes have been proposed for this purpose.

The first was proposed by Proust. It consisted in pouring a solution of muriate of tin into a decoction of galls: an abundant yellowish precipitate forms, which consists of the tannin in combination with oxide of tin: to separate the latter, the precipitate, after having been washed, is to be diffused in water, through which a current of sulphuretted hydrogen is to be passed: the sulphuretted oxide falls down, and the pure tanning principle remains in solution in the water *. This process is however exceptionable. Proust himself has since remarked †, that the muriatic acid retains a portion of the compound of tannin and oxide of tin in solution, so that all the tannin is not procured; and even what is obtained is not pure, as the muriate of tin precipitates likewise the extractive matter contained in the vegetable infusion.

Another process which he afterwards proposed, is to pour a solution of carbonate of potassa into an infusion of galls. A yellowish white coagulum is formed, which it is only necessary to wash with a little cold water to obtain the tannin, the coagulum being this substance separated from its solution by the affinity exerted by the alkaline carbonate to the water in which it was dissolved. Care must be taken not to wash it with too much water, by which it would be dissolved; nor with warm water: for the same reason a strong infusion of galls must be operated on. And it is not less essential, that the alkali should be saturated with carbonic acid, as the pure alkali favours its solution ‡. This process, however, is altogether inadmissible, as it is not pure tannin that is thus precipitated. Mr Davy found, that it is not possessed of the properties of that principle: it has not the astringent taste, is but slightly soluble in cold water, or in alkohol; and its solution acts little on gelatin, until it is saturated with an acid: it appeared, from his experiments, to consist of tannin and gallic acid, with carbonates of potassa and lime. A similar process has been more lately proposed

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* Nicholson's Journal, 4to, vol. xx. p. 338.

† Ibid. 8vo. vol. ii. p. 198. ‡ Ibid. 4to. vol. iv. p. 351.

by Bouillon Lagrange,—adding to an infusion of galls a solution of crystallized carbonate of ammonia, as long as there is any precipitation. The precipitate is washed with cold water until the water pass off without colour: it is then digested in pure alkohol, until the alkohol ceases to redden infusion of litmus: the residuum he considers as pure tannin*. This process seems, however, nearly equally liable to objection with the other.

A third process was proposed by Proust. Dizé had observed, that, by pouring sulphuric or muriatic acid on a strong decoction of galls, a considerable deposite is formed. According to Proust, this precipitate consists of the tannin in combination with the acid. It is washed with cold water; is dissolved in boiling water: the sulphuric acid is saturated by an alkaline carbonate, and the tannin is precipitated. It is washed with cold water †. It is still to be questioned, however, if, as obtained in this manner, it can be considered as pure: Mr Davy has remarked, that as extractive matter is likewise precipitated by these acids, a portion of it may be contained in this precipitate; and, from his experiments, it appeared also to contain a quantity of gallic acid.

Another method has been proposed by Merat Guillot. It consists in adding, to a solution containing tannin, lime-water: a precipitate is obtained in considerable quantity, which appears to consist of the tannin combined with lime. If it be treated with nitric or muriatic acid diluted with water, an effervescence takes place, the acid combines with the lime, and a matter so sparingly soluble as to remain on the filtre is obtained, which this chemist considered as pure tannin *. Mr Davy has supposed, that it must contain, besides tannin, some of the extractive matter of the bark, and that it may likewise contain saline matter. It is, however, the simplest process, and perhaps even affords purer tannin than the others; though a process is still wanting by which we can be certain of obtaining this principle in a state of perfect purity.

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* Annales de Chimie, tom. lvi. p. 187.

† Nicholson's Journal, 4to, vol. iv. p. 352.

Tannin, in the states in which it has been hitherto procured, may, by evaporation of its solution, be obtained in the solid form. It appears either as a loose powder, or a dry friable matter, having a resinous-like fracture. It is of a brown colour, or, according to Lagrange, of a white, which becomes brown only from exposure to the air; has a peculiar smell, and a taste rough and bitter.

This principle is soluble in water, either cold or warm. Its solution is of a brown colour, and retains the peculiar smell of the tannin. It is generally considered as being also soluble in alkohol; but according to Richter, this is only when the alkohol contains some water; for when highly rectified, it is scarcely at all soluble in it †.

Tannin appears, from Seguin's experiments, to be susceptible of oxygenizement. When its watery solution is exposed to the air, its surface acquires a fine pellicle, which becomes thicker the longer the fluid is exposed. If it be broken, it is soon renewed, and, from accumulating, it at length precipitates. It is quickly formed by exposure to oxygen, or to oxymuriatic acid, so much so, ac-

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* Nicholson's Journal, 8vo, vol. ii. p. 71.

† Philosophical Magazine, vol. xxiii. p. 73.

cording to Seguin, that, from merely bringing a bottle containing this acid into the vicinity of the infusion of tannin, a pellicle is instantly formed, which thickens rapidly, and at length precipitates *. As phenomena somewhat similar are exhibited, however, by infusions of vegetables which contain no tannin, it is not impossible but that they may arise from the extractive matter contained in the vegetable astringent from which the infusion of tannin had been prepared. This appears to be confirmed by the observation made by Seguin himself, that the infusion of tannin may be kept a long time without its properties being sensibly altered, and this even though it be not carefully secluded from the air. Lagrange, however, in his late examination of tannin, has affirmed, that it is very susceptible of oxygenizement, and that by this change it acquires the property of reddening litmus, which otherwise does not belong to it. It is very little liable to pass into a putrid state, and it forms a powerful antiseptic.

Tannin is thrown down from its solutions by several of the acids. Sulphuric acid causes a dense whitish precipitate. The residual liquor separated by filtration was found by Mr Davy still to precipitate gelatin, and therefore contained a portion of tannin. Muriatic acid produces similar effects, two compounds of the tannin being formed; one with an excess of acid which remains in solution, the other containing much tannin, which is precipitated. Nitric acid, when concentrated, first renders the solution turbid; but the solid matter, from the production of which this arises, is soon re-dissolved with efferves-

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[*] Nicholson's Journal, 4to, vol. i. p. 275.

cence, and the liquor becomes clear, and of an orange colour. The tannin is entirely decomposed during this action; for the liquid, after it, gives no precipitate with gelatin, even when the acid is saturated with an alkali. With dilute nitric acid a permanent precipitate is formed, and the residual liquid appears, from the test of gelatin, still to contain a portion of tannin. Lagrange has stated, that tannin prepared by the process which he has given, already described, is converted by oxymuriatic acid into gallic acid *. Were this established, it would point out the relation which appears to be so intimate between these two principles; and it might even lead to the suspicion, which some other facts suggest, that, in the processes to which they are subjected, the one is often converted into the other. It may be doubted, however, if this relation is so simple, as that gallic acid is merely tannin oxygenized.

The alkalis combine with tannin. A solution of pure potassa, poured into an infusion of galls, causes first a faint turbid appearance; but, by agitation, the fluid becomes clear, and its colour changes from yellowish brown to brownish red. The solution of gelatin does not act on the liquid in this state of combination, until an acid be added in excess, and then a copious precipitation is occasioned. The action of soda is precisely similar; as is that of ammonia. On heating the infusion to which ammonia has been added, part of the alkali is volatilized, and the remaining portion acts on tannin, forming a quantity of insoluble matter, and leaving little in solution †.

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* Annales de Chimie, tom. lvi. p. 191.

† Davy, Philosophical Transactions, 1803.

Lime, barytes, and strontites, in solution in water, appear likewise to combine with tannin, and to form compounds of sparing solubility; since, when added to infusion of galls, a precipitation ensues, and the residual liquor gives no precipitate with gelatin. The precipitate of these earths with pure tannin is, according to Lagrange, of a green colour. Magnesia boiled in such an infusion forms a deep green fluid, which does not precipitate the solution of gelatin: the magnesia acquires a grey colour, and appears to have abstracted the tannin. The action of argil, in an experiment performed in the same manner, appears to be precisely similar *.

The alkaline carbonates cause a precipitation of tannin, from the infusion of a vegetable astringent; but, as has already been remarked, this precipitate is not pure tannin, but contains a portion of the alkaline carbonate, and, in consequence of this, does not act on gelatin, until the alkali be saturated by an acid. The residual fluid of the infusion, acted on by the carbonate, still contains tannin, which appears to be combined with a large quantity of the alkali, so as to remain soluble; and it is equally incapable of acting on gelatin, until the alkali is saturated by an acid. The carbonates of lime, magnesia, and barytes, produce, in like manner, an insoluble combination of these respective earths with tannin: the residual liquid does not affect gelatin, even when an acid has been added to it; and hence there is no soluble combination of tannin formed in this case, as there is in that of the alkaline carbonates †.

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* Davy, Philosophical Transactions, 1803. † Ibid.

Even a number of neutral salts, as nitrate of potassa, muriate of soda, muriate of barytes, &c. cause a precipitation of tannin. This, Proust supposed to be owing merely to their combining with the water, which holds this principle dissolved. Mr Davy found reason to conclude, however, that these precipitates are not pure tannin, as this hypothesis implies, but contain a portion of the salt by which they had been thrown down.

The metallic oxides appear to have an affinity to tannin, and to combine with it, forming compounds in general insoluble. Mr Davy found, that when oxide of tin, or oxide of zinc, was boiled with infusion of galls for two hours, it became colourless, and seemed to be pure water, while the oxides gained a tint of dull yellow: and on dissolving them in muriatic acid, the solution acquired the property of precipitating copiously the solution of gelatin. In consequence of these affinities of the metallic oxides to this principle, many of the metallic salts act upon it: they in general give rise to dense coloured precipitates, which appear to consist of the tannin united with the metallic oxide, retaining perhaps, as Mr Davy has found some reason to suppose, a portion of the acid with which it was combined. Acetite of lead forms a precipitate of a grey colout ; nitrate of mercury, one that is yellow ; sulphate of manganese is thrown down green : but these precipitates generally change their colour in drying *.

The action of this principle on sulphate of iron is important, from its relation to the art of dyeing, and to the composition of ink: On the green sulphate of iron it has

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* Lagrange, Annales de Chimie, tom. lvi. p. 196.

no sensible action; but with the red sulphate, it gives a copious dense precipitate, of a dark blue colour, approaching to black when dried, and very different from that with the gallic acid, which is of great tenuity, so as to remain long suspended, and is perfectly black. In this action of tannin on the red sulphate, part of the oxygen is attracted by the tannin, so that the oxide passes to the state in which it exists in the green sulphate *. The deep black colour, produced by the action of vegetable astringents on the red sulphate of iron, appears to arise from the action both of the gallic acid and tannin; they combine with the oxide of iron; the precipitate is kept dissolved in some measure by the free sulphuric acid disengaged: and it is this which forms the colouring matter of ink, and of the black dyes.

The most characteristic, and perhaps the most important chemical property of this principle, is its power of combining with animal gelatin. When the solution of this principle is added to an infusion containing tannin, a copious soft precipitate, which quickly becomes flocculent, of a yellowish colour, is formed, and soon subsides: it is not putrescible; and on drying, contracts and becomes hard and brittle, but resumes its softness, and a degree of tenacity which it has, when it is moistened. The gelatin requires to be recently prepared: the quantity of precipitate is influenced by the state of concentration; the same quantities giving rather more precipitate, when strong solutions of them are mixed together. It is also influenced by the proportions; an excess of gelatin

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† Proust, Nicholson's Journal, 4to, vol. ii. p. 339.

redissolving a little of the precipitate. These circumstances require to be attended to, in estimating, by the test of gelatin, the quantity of tannin in any astringent, and *vice versâ* in using tannin as a test of gelatin. The tannin of different vegetables was found, by Mr Davy, to require different proportions of gelatin. On an average, 100 grains of the compound of gelatin and tannin, formed by precipitation from saturated solutions, contain about 54 grains of gelatin, and 46 of tannin.

Gelatin, even in an indurated or compact state, is capable of combining with tannin. A piece of animal skin, which consists principally of gelatin, immersed in an infusion containing tannin, discolours it in a short time, by attracting the tannin.

Tannin exposed to heat, affords an acid liquor, a brownish oil, and a considerable quantity of carbonic acid; leaving in the retort a light spongy coal *.

This principle, it has been remarked, exists in many vegetables, and always in a state of intermixture with other principles, particularly with gallic acid, extract, and mucilage. Seguin has remarked, that the gallic acid is often found unaccompanied by the tanning principle, as in cinchona, crude or roasted coffee, the roots of the strawberry plant, milfoil, scrofularia, arnica, and a number of others; these forming a dark precipitate with sulphate of iron, but not being affected by gelatin. Tannin, on the other hand, is, according to this chemist, never found alone, but always accompanied with the gallic acid. It exists not merely in the gall nut, oak bark, and sumach, the substances used in tanning, but abundantly in bistort, tormentil, rhubarb, squil, several species of pine, the acacias, and a number of other vegetables.

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* Seguin, Nicholson's Journal, 4to, vol. i. p. 274.

Mr Davy undertook the examination of the principal astringents, with the view of determining the proportion of tannin they contain, and the principles with which it is united *. In gall nuts, tannin is the principle present in by far the largest proportion : 500 grains of Aleppo galls yielded to water, by lixiviation, 185 grains of solid matter ; of which 130 were tannin, 31 gallic acid, 12 mucilage and extract, and 12 calcareous earth and saline matter. Oak bark affords a considerable proportion, though of course much less, from the quantity of fibrous matter in the bark : an ounce or 480 grains of the interior white bark afforded about 111 grains of solid matter by lixiviation, of which 77 were tannin. The bark of the Leicester willow afforded about the same quantity ; that of the Spanish chesnut less ; and the common willow and elm a much inferior proportion. Sumach afforded as much as oak bark. Souchong and green tea gave also a considerable quantity. The quantities vary according to the age of the tree, and also according to the season, as the experiments of Mr Biggin † have shown. The inner bark, Mr Davy found, always contained a larger proportion than the outer layers ; and as the interior layers are comparatively most abundant in young trees, their barks contain, in the same weight, a larger proportion of tannin than those of old trees.

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* Philosophical Transactions, 1803.

† Ibid. 1799, p. 299.

The substance named Catechu, obtained by decoction and inspissation from the wood of the Mimosa catechu, a native of India, is a very strong astringent, and, from Mr Davy's experiments, it appears to contain a large proportion of tannin. This substance is almost wholly soluble in water: a considerable proportion of it is also soluble in alkohol, but, when acted on by the latter fluid, a portion of mucilage remains undissolved. One hundred grains of what is named the Bombay Catechu consists, according to these experiments, of 54.5 of tannin, 34 of extractive matter, 6.5 mucilage, and 5 residual matter, chiefly impurities. The same quantity of the Bengal catechu gave 48.5 of tannin, 36.5 of extract, 8 of mucilage, and 7 of residual matter.

Another very astringent substance, known in the shops by the name of Kino, appears, according to the account of it given by Dr Duncan and by Vauquelin, to consist chiefly of a variety of tannin. It was first imported from Africa, and was said to be the produce, by exudation, of a particular tree. Dr Duncan has observed, however *, that it has every appearance of an extract obtained by decoction and inspissation, and that part of the kino of commerce, not distinguishable from that from Africa, is imported from Jamaica, and is known to be the extract of an astringent bark, that of the Coccoloba urifera. Its solution gives a copious precipitate with gelatin, and throws down also coloured precipitates from the metallic salts: that from the salts of iron is of a deep green colour. According to Vauquelin's experiments on it †, it consists

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* Edinburgh Dispensatory, p. 242.

† Nicholson's Journal, vol. vi. p. 232.

chiefly of tannin, with a proportion of mucilaginous or extractive matter. The kino examined by this chemist Dr Duncan suspects to be the substance named the Botany Bay Gum, which is the produce of different species of *eucalyptus*, and which forms at present the finest kino of the shops *.

Proust remarked, that the tannin afforded by different vegetables is not altogether uniform in its qualities,—an observation which is sufficiently confirmed by experiment. Thus, the tannin of catechu, in precipitating gelatin, does not form with it a magma of the consistence or insolubility of that formed by the tannin of galls: it gives also a violet-coloured ink with sulphate of iron. The tannin of kino forms with the solution of glue a rose-coloured coagulum, and does not precipitate the salts of iron black, but of a beautiful deep green colour, scarcely alterable by exposure to the air,—a property which also belongs to the tannin of rhubarb. The tannin of sumach, in precipitating glue, affords a white magma without consistence. From such facts, Proust concluded, that tannin has its varieties, like the other immediate principles of vegetables; the property of precipitating gelatin being that which unites them, and as it were constitutes the species †.

On this subject Mr Davy has observed, that the specific agencies of tannin, in all the different vegetable astringents, are the same. In every instance it is capable of entering into union with the acids, alkalis, and earths, and of forming insoluble compounds with gelatin and with skin; and he seems disposed to conclude, that although the opinion of Proust is sufficiently conformable to the facts generally known concerning the nature of the substances which are produced in organized matter, it cannot be considered as proved, till the tannin in different vegetables be examined in its pure and insulated state. In all the vegetable infusions in which it has been subjected to experiment, it exists in a state of union with other principles, by which its properties must be necessarily modified. Thus, as Mr Davy has remarked, the infusion of sumach owes its characteristic property of being precipitated by the caustic alkalis to the presence of sulphate of lime; and to this also may be owing the white colour of its precipitate with glue. That the infusion of galls is rendered green by the alkaline carbonates, evidently depends on the large quantity of gallic acid it contains; and that the solutions of catechu do not copiously precipitate the carbonated alkalis, appears to depend on their containing tannin in a peculiar state of union with extractive matter, and uncombined with gallic acid or earthy salts *.

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* Nicholson's Journal, 8vo, vol. vi. p. 234.

† Ibid. vol. ii. p. 201.

These observations are undoubtedly just; yet as tannin appears susceptible of alteration in its constitution, particularly from oxygenizement, it is not improbable, that slight variations of this kind may give rise to some of the differences observed in its properties,—a supposition confirmed by the discoveries with regard to its artificial form-

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* Philosophical Transactions, 1803.

ation, in which it is produced with properties somewhat different, so as to form at least three varieties.

The artificial formation of tannin, a subject highly interesting, has been amply investigated by Mr Hatchet, by whom it was discovered. It had been observed by Seguin, Proust, and Davy, that the tanning principle is developed in many vegetables by heat; and Mr Chenevix, in submitting coffee to chemical examination, found, that, by roasting it, tannin is evolved or produced: previous to roasting, it contains a principle somewhat analogous, but which does not precipitate gelatin, but, after it has been submitted to that process, its decoction gives an immediate precipitate *. The observation of these facts, however, did not lead to any farther investigation of the subject.

Mr Hatchet having observed in his experiments on lac, and some of the resins, the powerful action that nitric acid exerts on them, and that a substance is produced by this action possessed of some peculiar properties, and which appeared carbonaceous, was induced to examine the effects of the action of this acid on the bitumens, coal and charcoal. He found, that by digesting these with a sand heat in nitric acid, 100 grains being used to one ounce of acid of the specific gravity of 1.4, and fresh portions of the acid being added as it was decomposed or dissipated, a solution was obtained, at the end of five or six days, of a dark brown colour, and which afforded,

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* Nicholson's Journal, 8vo, vol. ii. p. 114.

when evaporated to dryness, a substance having the general properties of tannin, and which very readily precipitated solutions of gelatin. 100 grains of vegetable charcoal yield about 114 grains of this matter in a dry state.

This substance Mr Hatchet found was best obtained from carbonaceous matter when this is uncombined with any principle but oxygen; and hence substances frequently did not produce the tanning matter when treated with nitric acid, as saw-dust and different varieties of coal, which, after having been charred and submitted to the same treatment as before, produced it copiously. The coal of animal matter was equally susceptible of being converted into tannin by this process. Isinglass charred afforded it, for example, in Mr Hatchet's experiments, and, as he remarked, thus established the curious fact, " that one portion of the skin of an animal may be made to convert another into leather."

In conformity to this effect of charring in favouring the production of tannin, Mr Hatchet found, too, that substances charred by sulphuric acid, afforded the artificial tannin when afterwards treated with nitric acid; and even in some cases, in his first experiments, a portion of it appeared to be formed by the continued action of the sulphuric acid, being separated from the insoluble matter by the action of alkohol. This he afterwards investigated more fully *, and found, that by digesting sulphuric acid on a number of resins, balsams, camphor, oil of turpentine, lintseed oil, olive oil, and wax, washing the residuum, and digesting it in alkohol; tanning matter was procured.

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* Philosophical Transactions, 1806.

In a second series of experiments *, Mr Hatchet found, that almost every vegetable substance might be made to afford tannin, by the repeated distillation of nitric acid from them without any previous charring. He thus procured it from all the resins which he tried, from a number of the gum resins, from the balsams, indigo, and several other varieties of vegetable matter; some affording it with more difficulty than others, or requiring more distillations of the acid, and affording it also in different quantities. Some even did not afford it, such as elemi, tacamahac, olibanum, sandarach, copaiba, mastich, myrrh, gamboge, and caoutchouc, though, had the distillation been more frequently repeated, Mr Hatchet supposed it probable they might have done so. Gum arabic, gum tragacanth, and manna, afforded oxalic acid, but no tannin.

The nature of the product of all these operations was assertained by the precipitate it gave with gelatin, and, in some cases by skin being tanned, or converted into leather by its operation. It resembled, too, in almost all its other properties, natural tannin. Its flavour was astringent: exposed to heat, it swelled, and gave a voluminous coal; it was speedily dissolved by cold water, and by alkohol. Its solution produced copious precipitates when added to solutions of muriate of tin, acetite of lead, and red sulphate of iron; that from the first being of a dark grey colour, those from the others brown. It precipitated gold in its metallic state from its solution. With the nitrate of lime, nitrate of barytes, and other

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* Philosophical Transactions, 1805.

earthy salts, it likewise gave precipitates. The alkalis at first deepened the colour of its solution, and then rendered it turbid. Sulphuric and muriatic acids throw down from its solution a copious brown precipitate, soluble in warm water, and still capable of precipitating gelatin *.

It thus appears, that artificial tannin may be formed from a number of vegetable substances, and by different processes. The products of these processes, though all possessed of the essential characters of natural tannin, differ somewhat in their properties from it and from each other. Mr Hatchet has marked three varieties,—the first, that which is produced by the action of nitric acid on any carbonaceous substance, vegetable, animal, or mineral; the second, that which is formed by distilling nitric acid from resins, balsams, and similar substances; and the third, that which is extracted by alkohol from a number of resins, camphor, &c. digested with sulphuric acid.

The first of these varieties approaches most nearly in its properties to natural tannin. It resembles it in its solubility in water and in alkohol; in its action on gelatin and on skin; in its effects on the metallic solutions, on the alkalis, and on the earths. The sulphuric and muriatic acids, too, affect its solution, as they do that of natural tannin; and the only marked difference between them is in their relation to nitric acid. This variety of artificial tannin owes its origin to the action of this acid, and is not changed by the continuance of that action. Mr Hatchet found, that it might be dis-

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Philosophical Transactions, 1805.

solved in strong nitric acid, the solution distilled until the whole of the acid came over, and this be repeated three times without the tanning matter having suffered any alteration in its properties; while natural tannin extracted from different vegetable astringents, galls, oak bark, sumach and others, was always destroyed by the action of this acid *. This forms a striking difference between these two substances.

The second variety of artificial tannin, is that formed from resins and some other substances, by the repeated action of nitric acid, favoured by a high temperature, or by distilling the acid repeatedly from them. It is not therefore so easily formed, and the quantity of it produced is also always less. Its formation, as Mr Hatchet has conjectured, probably depends on the oxygen of the acid attracting the hydrogen of the resin, and forming water, and thus leaving an excess of carbon, which is then acted on by the acid, so as to be converted into tannin, in nearly the same manner that charcoal is. There is a slight difference, however, between this and the first variety, particularly in the precipitates which it forms with gelatin, which are always of a yellow colour, pale or deep, while those formed by the other are constantly brown; whence he concludes, that the different colours of the pre-

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* Some of these kinds of natural tannin resisted the action of nitric acid longer than others, such as that from oak bark; and those seemed most easily destroyed which had an intermixture of mucilage. Mr Hatchet was hence induced to add gum, and also sugar, to the artificial tannin, in subjecting it to the action of nitric acid, wit the view of promoting its decomposition, but without any effect.

cipitates depend on the state of the carbon of the tannin.

The third variety produced by the action of sulphuric acid on resins, balsams, and similar substances, is inferior, in the energy of its action on gelatin and skin, to the first variety; it is converted into it, by the action of nitric acid. By the continuance of the action of sulphuric acid, it is decomposed and converted into coal.

The first variety of tannin afforded, when decomposed by heat, products analogous to those of animal matter. First a little water, with a small quantity of nitric acid came over, then a small portion of a yellowish oil: on raising the heat, a large quantity of elastic fluid came over suddenly, which was principally ammonia; and carbonic acid gas, with a little nitrogen, were afterwards slowly disengaged. A bulky coal remained, which on incineration afforded a little lime. Carbon therefore appears to be its basis, with which are combined oxygen, hydrogen, and nitrogen. The third variety, Mr Hatchet remarks, from the mode of its formation, does not appear to contain nitrogen; and this, he adds, may perhaps be the cause of its less powerful action.

From the facility with which some vegetable substances, after being charred, are converted into tannin by nitric acid, Mr Hatchet supposes, that some such method may be economically employed in practice. After extracting the tannin from oak bark, by repeated maceration in different portions of water, the remaining matter was dried and moderately roasted. It was then moistened with diluted nitric acid, which was evaporated in a heat not much exceeding 300°, until the bark became dry. This was digested in water, and speedily formed a yellowish brown liquor, which abundantly precipitated gelatin. The operation was repeated on the residual bark with the same result; so that it might evidently have been continued until the whole of the bark had been converted into tannin. Peat, which consists of vegetable matter in a carbonized state, affords a large quantity of tannin, by such a process, with great facility; and the tanning quality of the water of peat moors, Mr Hatchet conjectures, may be derived from some spontaneous change of a similar nature*.

THE art of tanning, or converting the skin of animals into leather, depends on the operation of the principle, the chemical history of which has now been given, and has been elucidated by the discoveries made with regard to it. Tanning is indeed nothing more than combining tannin with the gelatin, which is the basis of the skin; and all the manipulations of the art, are directed to facilitate or effect this combination. A concise account of these, I take principally from a memoir by Mr Davy on this subject †.

The skin requires to be prepared for the action of the tanning liquor, by freeing it from the hair and other extraneous matter. This is done by washing it, and in some cases by inducing a slight degree of putrefaction, by which the epidermis is loosened, and the hair more easily detached. This is more generally effected, however, by the action of lime: the lime being diffused in water, and the skin steeped in it: its agency, from Mr Davy's investigation of the subject, appears to depend on the lime combining with the cuticle, and forming an insoluble compound, which is loose and friable. The fat and oily matter adhering to the skin, form with the lime, too, saponaceous compounds, and are thus removed.

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* Philosophical Transactions, 1806.

† Journals of the Royal Institution.

After the skin has been cleaned, it is submitted to other operations, before it is immersed in the tan liquor. According to Mr Davy's account of the practices of the art, the large and thick hides which have undergone incipient putrefaction, are introduced for a short time into a strong infusion of oak bark, and after this they are acted on by water impregnated with a little sulphuric or acetic acid, in consequence of which they become harder and denser than before, and fitted, after being tanned, for the purpose of forming the stouter kinds of sole leather. The lighter and thinner skins are treated in a different manner: they are macerated for some days, in a ley formed from the infusion of pigeons dung in water, which contains a little carbonate of ammonia; the skin is thus deprived of its elasticity, and becomes more soft.

The tanning liquor is, in this country, generally prepared by infusing bruised oak bark in water: and skins are tanned, by being successively immersed in such infusions, saturated in different degrees with the astringent principles of the bark. The first leys in which they are immersed are weak, but towards the completion of the process they are used as strong as possible; and in preparing stout sole leather, the skins are kept in an ooze, approaching to saturation, by means of layers of oak bark.

The infusion of oak bark, especially that obtained by the first maceration, contains principally tannin and extractive matter; any gallic acid, if present, as has been supposed, being at least in inconsiderable proportion. In the course of the maceration of the skins in these liquors, the tannin combines gradually with the gelatin, which, in an organized form, principally constitutes the skin, and forms with it a compound insoluble in water, dense and impermeable to that fluid, while it possesses at the same time a certain degree of elasticity. The extractive matter also enters into the combination; for when skin in large quantity has exerted its full action on a small quantity of infusion, it at length abstracts the whole dissolved matter, and renders it colourless. From this extractive matter colour is derived, and the skin may perhaps be rendered more dense.

It has been supposed, that the gallic acid frequently contained in vegetable astringents, facilitates the action of their tannin, in converting skin into leather. According to the theory of the operation, as given by Seguin *, skin is gelatin in a hardened state, from slight oxidizement; the gallic acid in some measure de-oxidizes it, and hence reduces it to that state in which it combines more easily with gelatin. There is little proof given, however, of this theory; and it appears sufficiently established, that the operation can be performed without the presence of this acid: and indeed in the tan liquor prepared by one ma-

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* Nicholson's Journal, 4to, vol. i. p. 277.

ceration from oak bark, it is scarcely discoverable, and, if it do exist in it, is in intimate combination with the extractive matter.

The operation of tanning, as now described, requires a number of months, from the skins being successively and slowly introduced into infusions of different degrees of strength. Seguin, after his discovery of tannin, proposed to abridge the process, by introducing the skins more speedily into strong infusions of the tanning substance; and in this way, according to the excellent report given on the art of tanning, by Pelletier and Lelievre *, in which his method is fully described, the whole could be finished in about twenty days, and leather obtained equal in quality to that prepared by the old method. There is reason, however, to doubt of the superiority of this new method. Mr Nicholson, in some observations on this subject, when a patent was taken out for Seguin's method in this country †, stated, that from information acquired from the manufacturers, he found that they had previously been sufficiently acquainted with the powers of the strong tanning infusions; and that it had even been proposed to employ them so as to abridge the process. But the leather thus prepared was by no means equal to that prepared in the old method. The advantage of the slow and gradual process, appears to be, that the whole substance of the skin is penetrated, and equally changed; while in the more rapid method the external parts must be more acted on; and the texture probably will be more

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* Mémoirs de Chimie de Pelletier, tom. ii. p. 357.

† Journal, 4to, vol. i. p. 26.

unequal. It appears also from Mr Davy's experiments, to combine with a larger quantity of the extractive matter contained in the astringent infusion; and hence too the advantage of the immersions in the weak liquors, as these contain more of this than the strong infusions. It must be confessed, however, that for any thing theory can discover, the common process appears to be unnecessarily protracted, and some advantage might probably be derived from adopting some of the manipulations of Seguin.

The skin in drying increases in weight, from the fixation of the vegetable matter: the quantity of this seldom exceeds one-third of its weight. The increase is greater, according to Mr Davy's experiments, from quick than from slow tanning. In the latter, he supposes more of the extractive matter enters into combination, and this, weakening the attraction of the skin to tannin, less of this is absorbed, and less vegetable matter on the whole enters into the composition of the leather. Probably also, in the slow process, more of the animal matter is removed.

Other substances are used in tanning, as the bark of the willow, elm, and other trees, and even galls and catechu. The leather prepared from these varies in colour, and in some other external qualities.

Another application of tannin is in the composition of writing ink. This is formed from a mixture of galls and sulphate of iron macerated in water, a quantity of gum arabic being added to prevent the liquid from being too thin and watery. It was imagined formerly, that the black colour was produced from the action of the gallic acid on the oxide of iron; but as this acid is much inferior to tannin in producing this colour, and as so much tannin exists in the gall nut, it is chiefly from this principle, in combination with the oxide of iron, that the colour must arise; the sulphuric acid probably contributing to the solubility of the compound. The iron requires, for the full production of this colour, to be at the maximum of oxidizement; and hence ink, when first prepared from the green sulphate, is of a paler colour than it afterwards assumes. The vegetable matter is liable to slow decomposition: hence the mouldiness of ink when it is long kept, and the decay of it by age, so that manuscripts at length become illegible. The colour may be in some measure restored in such a case, by spreading over the paper a dilute infusion of galls; or a blue colour may be produced, of course marking the letters, by using a dilute solution of an alkaline prussiate. On this subject, some observations were made by Blagden *.

Tannin must also be regarded as the basis of the black dyes, these being obtained from sulphate of iron, acted on by infusions of galls, or other astringents.

Tannin, it has been supposed, as a test of gelatin, may sometimes afford information of some importance in cases of morbid affection, as it can discover the presence of that principle, and even its quantity in any of the secreted fluids.

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* Philosophical Transactions, vol. lxxvii. p. 451.

SECT. XV.

GALLIC ACID.

THERE exist in the juices of many vegetables, especially in their fruits, at certain states of maturity, compounds possessed of the general acid properties: And such acids are likewise found combined with some of the proximate vegetable principles; or sometimes united with the alkalis or earths, forming what have been named the Essential Salts of Plants. These native vegetable acids have been classed together; and they no doubt possess a certain resemblance in their properties, and in their chemical composition. They are not however to be regarded as mere varieties of a species: each forms a species, or peculiar proximate principle, perfectly distinct, and with differences as important as exist among the other immediate principles of plants. Seven acids of this kind have been distinguished,—the Gallic, Citric, Malic, Oxalic, Tartaric, Benzoic, and Acetic. To these may perhaps be added the Moroxylic acid, which has been more recently distinguished.

These acids are of similar composition: they have all a compound base of carbon and hydrogen existing in each in certain proportions, and acidified by oxygen; hence, by subjecting them to operations in which the proportions are altered, they are sometimes converted into each other. The malic, citric, gallic, and perhaps some of the others, are thus convertible into the oxalic. This conversion is effected by the action of substances communicating oxygen, and may arise either from an additional proportion of oxygen entering into the combination, or from a portion of hydrogen or carbon being abstracted. When subjected to destructive distillation, they afford a large quantity of empyreumatic acetic acid; and they are probably to be regarded as the most highly oxygenized of the vegetable products.

The GALLIC ACID, the history of which is to be given in this section, it has appeared from the history of tannin, has an intimate connection with that principle. They generally exist together, and either of them seldom is found in any vegetable without a portion of the other. There are some plants, however, as has been remarked under the history of tannin, which are said to contain the gallic acid alone.

This acid exists in largest quantity in the gall nut, whence it has received its name. The infusion of this substance, it had been observed by the Dijon Academicians, has some of the properties of an acid: it reddens the infusion of litmus; and they farther found, that this principle is raised by distillation, the product of this operation striking a black colour with salts of iron; and that its solution in water precipitates the alkaline sulphurets, and decomposes metallic solutions *. Scheele first obtained this acid, however, in a pure form, and described its properties. He observed, that an infusion of galls had deposited a sediment of a grey colour, and of a crystalline

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* Elemens de Chimie, tom. iii.

appearance, which had an acid but not astringent taste, and which precipitated sulphate of iron black. To investigate the nature of this salt, he allowed a strong infusion of galls to remain in a vessel imperfectly closed for some months. A thick mould was at first formed on its surface; its astringent taste diminished, and its sourness increased. A sediment was at length collected at the bottom: this was washed with cold water, and then as much boiling water poured on it as was sufficient to dissolve it. On evaporating the filtered solution by a gentle heat, a salt was obtained, partly in the form of a fine sand, and partly in the form of radiated crystals, of a grey colour which was not removed by repeated solutions and crystallizations. This substance is the Gallic Acid *.

Other methods have since been employed to obtain it, less tedious, and affording it, perhaps, in a state of rather greater purity. Scheele observed, that when galls are distilled with a strong heat, an acid liquor first passes over, and afterwards a saline matter rises, possessed of all the properties of gallic acid. This method has been employed by Deyeux; heat being slowly applied to powdered gall nuts in a glass retort. At first a limpid fluid condenses in the receiver, and afterwards crystals of a white colour condense in the upper part of the vessel: the heat is stopt whenever the crystals towards the lower part begin to melt, as, if continued longer, a portion of oil is volatilized, and renders them impure. This process, as Mr Davy has remarked †, is the most simple, and least ex-

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* Crell's Chemical Journal, vol. i. p. 24.

† Journals of the Royal Institution, vol. i. p. 275.

pensive; and perhaps scarcely any other need to be employed.

Several others, however, have been proposed. Mr Davy found, that when carbonate of barytes is boiled for some time with an infusion of gall nut, it affords a bluish green liquor, which appears, from the common tests, to contain neither tannin nor extract. When diluted sulphuric acid is dropt into this liquor, it becomes turbid; sulphate of barytes is precipitated; and, after filtration, if the saturation of the earth be perfect, a colourless solution, apparently pure, is obtained *. Mr Fiedler has employed the affinity of another earth, argil, to tannin and extractive matter, to abstract them from the gallic acid of the infusion of galls. He boils an ounce of galls in sixteen ounces of water, until half the quantity of liquid is evaporated: he adds to this the quantity of argil which is obtained from the decomposition of two ounces of alum by an alkaline solution, agitating them frequently. After twenty-four hours, the liquor being filtered, passed colourless,—a proof that the extract had been abstracted; and it was not rendered turbid by solution of gelatin,—a proof that the tannin had also been removed. This liquor being concentrated by evaporation, afforded the pure gallic acid in acicular crystals †. This process was performed by Mr Davy, but without perfect success; the filtered liquor, when the argil had not been boiled with it, still giving a slight precipitate with gelatin, while, when it had been boiled, the greater part of the gallic acid, as well as of

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* Journals of the Royal Institution, vol. i. p. 274.

† Nicholson's Journal, 8vo, vol. i. p. 237.

the other principles, had been abstracted. Proust has employed the affinity of oxide of tin for the same purpose: dropping muriate of tin into the solution of the acid, as it is obtained by the first process of Scheele, while any flocculi precipitate, and, from evaporation of the filtered liquor, a voluminous mass of white and brilliant crystals are obtained *. Richter has given another process, in which an infusion of galls in cold water is evaporated to dryness. Pure alkohol is poured on the dry matter: it dissolves the gallic acid, and leaves the tannin undissolved: the alkohol is distilled from the solution to nearly a solid mass. Water is added to this, and a gentle heat applied. A solution, clear, and almost colourless, is obtained, which, by evaporation, affords small white prismatic crystals of gallic acid, about half an ounce of them being obtained from a pound of galls †. The process, however, is liable to inaccuracy; for, if the alkohol is not very highly rectified, a portion of the tannin will likewise be dissolved; and perhaps it is to be suspected, that, in any method of performing it, a small quantity of this principle will be taken up, and will adhere to the gallic acid.

This acid, when obtained pure, is in slender prisms of a perfectly white colour, which suffer no change from exposure to the air: its taste is sour, and its solution reddens the vegetable colours, and excites effervescence with the alkaline carbonates.

It is soluble, according to Scheele's experiments, in its weight and a half of boiling water: the solution, as it

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* Journal de Physique, tom. lxi. p. 117.

† Philosophical Magazine, vol. xxiii. p. 74.

cools, becomes turbid, from the formation of small crystals; and it requires 24 parts of cold water for its solution. It is much more soluble in alkohol: it dissolves in its own weight when the alkohol is boiling, and requires about four parts when the alkohol is cold.

When exposed to heat, it fuses, giving an agreeable odour, and leaving a hard coal, which is with difficulty reduced to ashes. When the operation is performed in a retort, after it has melted, an acid liquor comes over, without any oil; and a portion of it at length sublimes, remaining fluid while the neck of the retort is hot, but shooting into crystals as it cools. A large quantity of charcoal remains in the retort. The sublimed acid appears to differ a little from the original one: it has nearly the same taste and odour as the acid of benzoin, but it retains the other characteristic properties of the acid. These facts were ascertained by Scheele. Deyeux farther found, that, during the decomposition of this acid by heat, an aëriform fluid is disengaged, which contains oxygen gas in larger proportion than atmospheric air; and that, by repeated distillations, or exposing always the quantity that sublimes anew to heat, it may be completely decomposed. He has concluded, that it consists of carbon and oxygen, since it is resolved into these in its decomposition; and that it contains more carbon than carbonic acid *. There can be no doubt, however, of hydrogen also existing in its composition, though the proportion of carbon it contains is undoubtedly large. Scheele found, that by treating it with nitric acid in the usual manner, it is converted into oxalic acid.

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* Annales de Chimie, tom. xvii.

This acid combines with the alkalis and earths, forming salts denominated Gallates, the properties of which have been very little examined. Richter has remarked, that the alkaline gallates form black precipitates with solutions of iron, and likewise precipitate all other metallic solutions. Its combinations with the alkaline earths have a considerable degree of solubility, so that, if the solutions are dilute, no precipitate appears when they are formed, especially if there be a slight excess of the acid. According to Proust, when gallic acid is saturated with the alkalis, it always gives liquors of a green colour; but as the acid itself is white, and as colourless acids do not produce with the alkalis coloured salts, this may probably be owing to foreign matter adhering to the acid which the saturation developes.

Scheele remarked, that gallic acid precipitates metals from their solutions of different colours; and he added several facts with regard to these precipitations. Its solution gives a dark green colour to a solution of gold, and makes it deposite by degrees a brown powder, which is gold revived. A solution of silver is rendered brown, and deposites, if warm, a grey powder, which is silver in its metallic state. A solution of mercury is precipitated of an orange yellow. A solution of copper yields a brown sediment. Acetated lead is precipitated of a white colour. Bismuth gives a lemon coloured precipitate. The acid of molybdæna becomes of a dark yellow, without any precipitation. Platina, zinc, the acid of arsenic, tin, cobalt, and the regulus of manganese, undergo no change *.

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* Crell's Chemical Journal, vol. i. p. 28.

Gallic acid gives a black colour with the salts of iron: the precipitate on which this depends is, as Proust has remarked, much finer, and remains longer suspended than that from tannin. In this action, the gallic acid appears to have nearly the same relation to the oxide that tannin has. When added to the solution of the pure and neutral green sulphate, it produces no change of colour immediately, but, from exposure to the air, the dark colour appears. According to Proust's view of the subject *, this is owing to the iron in the green sulphate not being sufficiently oxidized to form the coloured compound; and exposure to the atmosphere produces the colour, by producing this higher oxidizement of the metal. Berthollet has contended, however, that other causes likewise operate in the production of this coloured combination, and that the theory of it is not so simple. He has remarked, that, if the acid has been added to the solution of the sulphate of iron without producing the dark colour, it immediately appears on large dilution with water, or on the addition of a little alkali without the contact of the air; or if a little iron-filings be put into a flask of the mixed solutions, colour is acquired rapidly, though their effect must be de-oxidizing. He supposes, therefore, that the gallic acid does not form the black coloured precipitate with the green sulphate of iron, not from the low state of oxidizement merely, but because the sulphuric acid has too much power over the black oxide, and retains it too strongly. But if the action of the sulphuric acid be weakened by a sufficient quantity of water, by an

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* Nicholson's Journal, 4to, vol. i. p. 458.

alkali, or by iron acting on it, then the oxide may combine with the gallic acid; and a higher degree of oxidizement, such as that which exists in the red sulphate, favours the combination, from the metal in that state having a less strong attraction to the sulphuric acid [*]. Richter has adopted the same views, and has maintained, that, when a solution of gallic acid immediately forms a black precipitate in neutral solutions of iron, it is not pure, and commonly contains tannin, which combines with the sulphuric acid, and separates from it the oxide of iron, which then combines with the gallic acid [†]. Berthollet admits, however, that highly oxidized iron produces a deeper black with gallic acid than iron in a lower degree of oxidizement,—an effect which he formerly supposed owing to the acid being partially decomposed, part of its hydrogen being attracted by the excess of oxygen in the oxide, and carbon being transferred to the imperfect oxide, with which the remaining acid then combines.

According to Proust, gallic acid dissolves tannin, or rather renders it more soluble in water. Partly from this, and partly from both principles forming compounds with oxide of iron of a black colour, arises the advantage derived from their combination in the formation of inks and black dyes, or the superiority of a mere infusion of a vegetable astringent containing both, as the gall nut, to the use of either in a purer state. These applications, which partly depend on the agency of gallic acid, have been already taken notice of under the history of tannin.

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[*] Chemical Statics, vol. ii. p. 232.

[†] Philosophical Magazine, vol. xxiii. p. 75.

SECT. XVI.

MALIC ACID.

SCHEELE, in examining the acid juices of unripe fruits, found that they consisted generally of two acids, mingled in different proportions; one, which, existing in abundance and in a pure state in the fruit of the lemon, he named Acid of Lemons, and which has since received the name of Citric Acid; the other, which, from composing principally the juice of unripe apples, he named Acid of Apples, and which has since received the appellation of Malic Acid. The fruit of the gooseberry, of currants, bilberries, beamberries, cherries, strawberries, cloudberries, and raspberries, contain nearly equal quantities of both acids: cranberries, whortleberries, birdcherries, and doghips, contain the citric, with little of the malic acid; while the juice of the barberry, elderberry, sloe, and plumb, consists of the malic acid, with little or no traces of the citric. It is probable, however, that the proportions of these in the same fruit will vary at different periods of vegetation, and may even be altered by culture and climate. The history of the Malic acid is first to be given.

The process which Scheele gave for its extraction is to saturate the expressed juice of unripe apples by the addition of carbonate of potassa: to the saturated liquid, acetite of lead is added, as long as there is any precipitation: the precipitate, which is the compound of malic acid and oxide of lead, is washed, and diluted sulphuric acid added, until the mixture has a perfectly acid taste, without any sweetness: the malic acid thus disengaged is then separated by filtration from the sulphate of lead *.

When it exists in fruits in combination with the citric acid, the process which Scheele employed to separate them, was to evaporate the expressed juice to the consistence of honey, and then dissolve it in alkohol: the mucilaginous matter was thus removed, and the two acids existed in the solution. This being filtrated, the alkohol was evaporated, and to the remaining acid fluid twice its weight of water was added. It was then saturated with chalk: the citric acid forms with the lime of the chalk an insoluble compound, which is precipitated, the precipitation being promoted by boiling the liquor a little. The compound of lime and malic acid which remained in solution was precipitated by alkohol, and washed with that fluid, to carry off any saccharine or other vegetable matter: the malate of lime was decomposed by the addition of acetite of lead, and the malate of lead thus obtained decomposed by sulphuric acid, as in the preceding process.

Malic acid, it was also found by Scheele, can be artificially formed. Sugar, it has already been stated, when acted on by nitric acid, is converted into oxalic acid; but Scheele observed, that in this process a quantity of malic acid is also produced. If the oxalic acid formed in that process be separated, by adding lime-water as long as there is any precipitation, there still remains in solution

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* Crell's Chemical Journal, vol. ii. p. 7.

another acid, which neither gives any indication of nitric acid, nor precipitates lime-water. This is the malic acid, which he separated by a process similar to that last described. It is probable, that the malic acid is the primary product of this operation, and that, as it is formed, part of it is converted, by the continued action of the nitric acid, into oxalic acid.

Scheele having discovered this fact, examined the results of the action of nitric acid on a number of other vegetable substances, and found, that various mucilages, fecula, and extractive substances, afforded it, generally with oxalic and sometimes with saccho-lactic acid. Essential oils yielded very little of either, and animal substances afforded portions of them only when acted on by concentrated nitrous acid. Oxymuriatic acid forms it from gums still more readily than nitric acid does.

Malic acid is not susceptible of crystallization. By this it is particularly distinguished from the other vegetable acids, and is also capable of being more easily detected when mixed with them, as it forms the uncrystallizable residue of the liquid from which they have crystallized. When much evaporated, it becomes thick and viscid. Its solution, when strong, is of a brownish red colour, has a very sour taste, and reddens immediately the vegetable colours.

When exposed to heat, it is easily decomposed: its colour darkens; it swells up, exhales an acrid vapour, and leaves a voluminous coal. When subjected to destructive distillation, the products are an acid liquid, much carbonic acid gas, with a portion of carburetted hydrogen, and charcoal. The acid thus formed, according to Fourcroy, appears to be the empyreumatic acetic, or, as it was named, pyro-mucous acid.

Malic acid, in the state of its watery solution, suffers, when kept, spontaneous decomposition.

It is decomposed by the more powerful acids.' Sulphuric acid chars it: nitric acid converts it into oxalic acid.

It unites with the alkalis and earths, forming salts denominated Malates, the properties of which have scarcely been examined but by Scheele. With the three alkalis it forms salts, which he remarks are deliquescent. With lime it forms a salt, when neutral, in small irregular crystals, which require a large quantity of boiling water for their solution; but when there is a slight excess of acid, they are readily soluble in cold water. In combining with barytes, the results are similar. By the comparative solubility of these combinations with this earth, it is easily distinguished from oxalic and some of the other vegetable acids. With argil it affords a neutral salt, which is not easily soluble in water; with magnesia, a deliquescent salt.

Malic acid acts on some of the metals. Scheele observed, that it dissolves iron and zinc: the solution of malate of iron is brown, and not crystallizable; that of zinc yields regular crystals. He adds, that upon the other metals it has no perceptible effect. It combines, however, with their oxides, and, in consequence of such combinations, causes precipitates in several of the metallic solutions. It precipitates, in particular, the nitrates of mercury, lead, and silver, by which it may be distinguished from citric acid, which does not occasion precipitation in these solutions. It also decomposes the solution of gold, and even reduces the oxide to the metallic state.

This acid is applied to no use.

SECT. XVII.

CITRIC ACID.

It is this acid which exists in the juice of the lemon and lime, and gives it its sourness. It is mixed, however, with mucilaginous and extractive matter; and we are indebted to Scheele for the first process by which the acid is obtained pure, and for the knowledge of its properties in this state.

He found, that it could not be obtained pure and crystallized by mère evaporation of the lemon juice, and that even the addition of alkohol did not separate completely the foreign matter. The process he followed is to saturate the expressed juice of the lemon, by the addition of chalk. The citric acid, combining with the lime, forms an insoluble compound, which of course precipitates. This is well washed with warm water, until the water pass off colourless; and in this way the mucilage and extractive matter are abstracted. The citrate of lime is then subjected, in a matrass, to the action of as much sulphuric acid, previously diluted, as is sufficient to saturate the lime of the quantity of chalk that has been employed. The citric acid is disengaged and dissolved by the water: the mixture is boiled for a few minutes, to facilitate the precipitation of the sulphate of lime, and is then filtered. The filtered liquor is evaporated to the consistence of syrup, any sulphate of lime separated during the evaporation being withdrawn; and, on cooling and standing for some time, the citric acid is obtained in needle-like crystals. Scheele found it useful to add a slight excess of sulphuric acid, which afterwards remained in the residual liquor; and Dizé, in some observations on this process [*], has remarked, that this is requisite to decompose and facilitate the separation of a portion of mucilage or extractive matter, which still adheres to the citric acid when it combines with the lime, and which, when the acid is afterwards disengaged, opposes its crystallization. This the free sulphuric acid chars towards the end of the evaporation. It is not improbable, however, but that the brown or even black colour which the acid assumes at that stage, when an excess of sulphuric acid is present, may be owing, as Mr Nicholson remarked, to the action of that acid on the citric acid itself; and Proust, in some observations on the process, has observed, that if too great an excess of sulphuric acid be used, this happens, and the evaporated fluid refuses even to crystallize [†]. He has added some facts with regard to the proportions that may be useful in conducting the process. Four ounces of chalk, saturated with lemon juice, required for the saturation 94 ounces; and from this 7½ ounces of dry citrate of lime were obtained. The four ounces of chalk required for its saturation 20 ounces of a diluted sulphuric acid, composed of one part of the common sulphuric acid, with three of water; and, of course, this is the quantity of that acid to be used in decomposing this quantity of citrate of lime.

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[*] Nicholson's Journal, 4to, vol. ii. p. 43.

[†] Philosophical Magazine, vol. x. p. 112.

Citric acid exists in a number of other fruits, from which it may be extracted, and much, I believe, of what is at present found in the shops, is prepared from the juice of the lime. From Vauquelin's analysis of the pulp of the tamarind *, it appears to be the chief acid constituent of that fruit; one pound of the common prepared pulp of the shops, containing an ounce and a half, with smaller quantities of malic and tartaric acids.

Citric acid obtained by a first crystallization, is not perfectly white, but it becomes so when the crystallization is repeated. Its crystals, when regular, which they are only when formed on a large scale, are rhomboidal prisms, acuminated by four planes. Its acid powers are very considerable: its taste is extremely sour, and almost caustic; and it instantly reddens the vegetable colours.

Exposed to heat, the crystals melt, from the solvent power of their water of crystallization; by the continuance of the heat, the acid suffers decomposition, exhales an acrid vapour, and is reduced to a coal. Subjected to destructive distillation, it affords an acid liquor, which appears to be the acetic, afterwards carbonic acid gas and carburetted hydrogen, leaving a light charcoal.

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* Annales de Chimie, tom. v. p. 104.

This acid is very soluble in water. At a moderate temperature, 100 parts of water dissolve, according to Vauquelin, 75 parts, cold being produced during the solution; at 212° it dissolves twice its weight of it. Like the other vegetable acids, its solution undergoes spontaneous decomposition, though not very readily.

The more powerful acids decompose it, though with some difficulty. Concentrated sulphuric acid converts it, according to Fourcroy, into acetic acid. Scheele remarked, that nitric acid did not convert it, as it did some of the other vegetable acids, into oxalic acid; but Fourcroy and Vauquelin have found, that when acted on by a large quantity of nitric acid for a long time, it affords a small portion of oxalic, with a larger portion of acetic acid.

Citric acid combines with the alkalis and earths, forming salts denominated Citrates; the properties of which have been examined with care by Vauquelin, the results of whose experiments have been stated by Fourcroy *.

The citrate of potassa is very soluble, and does not crystallize but with difficulty, and is deliquescent: its taste is purely saline, and rather mild. It contains 55.55 of acid, and 44.45 of alkali. Citrate of soda is likewise very soluble, requiring little more than its weight of water for its solution: it crystallizes in six-sided prisms, and the crystals are slightly efflorescent. Their taste is faintly saline: the proportions of the solid salt are 60.7 of acid, and 39.3 of soda. Citrate of ammonia is equally or even more soluble than the others, and does not crystallize but when its solution is much concentrated: the form of its

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* System of Chemical Knowledge, vol. vii. p. 282.

crystals is an elongated prism. It consists of 62 of acid, and 38 of ammonia.

The earthy citrates are in general less soluble. When the solution of barytes is poured into the acid, a precipitate, soluble in the liquid by agitation, is formed; when the whole is saturated, the salt is deposited at first in the form of a powder, which is covered afterwards with a kind of crystalline efflorescence, and which a large quantity of water dissolves. It consists of 50 of acid, and 50 of base. When the citric acid is saturated by lime, small crystals are deposited, which are very sparingly soluble: 100 parts contain 62.66 of acid, and 37.34 of lime. When saturated by magnesia, the concentrated solution does not easily crystallize regularly, but rather assumes the state of a white, opaque, and somewhat spongy salt. The proportions of the salt, are 66.66 of acid, and 33.34 of base.

Vauquelin has likewise examined the action of citric acid on the metals. It does not dissolve silver, but it combines with its oxide, and forms a salt insoluble, of a harsh and strong metallic taste, and which, like the other salts of silver, is blackened by light: it is also decomposed by heat, leaving metallic silver intermixed with charcoal. It consists of 36 of acid, and 64 of oxide. Quicksilver is scarcely more acted on by citric acid, but its oxide combines with it: the red oxide, when added to the acid, causes an effervescence, and becomes white and solid: the salt is not perceptibly soluble in water, but is decomposed by it, the water becoming milky. It is decomposed by heat, and the oxide is reduced. Zinc is dissolved readily by a solution of citric acid, hydrogen gas being disengaged; and the solution, after some hours, deposites small brilliant crystals insoluble in water: 100 parts of this salt contain nearly equal parts of acid and oxide. Iron is dissolved nearly in the same manner: the solution is of a brown colour, and by spontaneous evaporation it deposites small crystals. Evaporated by heat, it becomes black and pulverulent. This salt is very soluble in water; its taste is very astringent: it consists of 30.38 of oxide, and 69.62 of acid.

As affording chemical characters by which this acid may be distinguished, it may be added, that solutions of the acetites of magnesia, lime, and argil; of the muriates of barytes, lime, argil, and magnesia; and of the nitrates and sulphates of these substances, undergo no apparent change from the addition of citric acid. The muriates and nitrates of zinc, the sulphate, muriate, nitrate, and acetite of copper, and the nitrate of lead, are not decomposed by it; but the acetite of lead gives immediately a precipitate of a white powder. The nitrate and acetite of mercury are also immediately decomposed, and a precipitate of a brick red colour thrown down. The acetite and sulphate of iron in solution, receive from it a green tinge *. All the alkaline citrates are precipitated by the solution of barytes: the precipitate which they form with calcareous salts, is soluble in less than 500 parts of water. The oxalic and tartaric acids decompose them, and form in their solutions crystallized or insoluble precipitates †.

Citric acid, in its crystallized state, can be preserved for

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* Dizé, Nicholson's Journal, 4to, vol. ii. p. 45.

† Vauquelin, Fourcroy's Chemistry, vol. vii. p. 286.

any length of time without decomposition; and a grateful lemonade may be prepared from it, by dissolving 30 or 40 grains in a pint of water, with the addition of a little sugar; and to communicate flavour, a little lemon peel, or powder formed by rubbing sugar on the fresh lemon. The lemon juice may be regarded as a specific in scurvy, and there is every probability that the crystallized citric acid may be equally effectual.

SECT. XVIII.

OXALIC ACID.

It has been long known, that a crystallized acid salt could be procured from the juice of some of the species of sorrel, particularly the Oxalis acetosella. Margraaf discovered the existence of potassa in this salt, and of course proved that it is not a pure acid; but the nature of the acid which it did contain, was for some time not well determined. Bergman discovered that sugar, when subjected to the action of nitric acid, affords an acid of a particular nature, the properties and combinations of which he examined; and some time afterwards, Scheele made the discovery, that the acid which exists in the salt of sorrel is precisely of the same nature; that it may be extracted from that salt and obtained pure; and that, on the other hand, a salt perfectly analogous to the salt of sorrel, may be formed by combining the acid prepared from sugar, with such a quantity of potassa as shall still leave an excess of acid. To this acid, thus existing in the vegetable kingdom, and capable also of being artificially formed, the name of Oxalic has been given.

The native salt of sorrel, the super-oxalate of potassa, is extracted from the juice of the sorrel, by the following process: The leaves of the plant are bruised with a little water, and the juice expressed; the impurities are allowed to subside, and the separation of any foreign matter is facilitated by heating it slightly: it is then clarified by adding to it water, in which a small portion of fine clay has been suspended, and with which it is agitated. The clarified juice is put into boilers of tinned copper, and is boiled gently, until a pellicle forms on its surface: it is then put aside for a month, in earthen vessels: a salt crystallizes on the sides of the vessel, of a greyish colour; and fresh quantities of this are obtained, by renewing the evaporation and clarification. The whole salt is then purified by a second crystallization, and is obtained perfectly white and well crystallized *. It is known in the shops under the name of Salt of Lemons, and is used principally for removing stains from ink. It is prepared in some districts of Switzerland and Germany.

Scheele obtained the acid from this salt, by adding to its solution in water a solution of acetate of lead prepared with distilled vinegar, as long as there is any precipitation. The precipitate is the oxalate of lead. It is washed with water, and decomposed by the addition of the due proportion of sulphuric acid; this being estimated

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* Annales de Chimie, tom. xiv. p. 7.

from the quantity of it, known by a previous experiment to be necessary for the decomposition of the quantity of acetate of lead employed. The oxalic acid remains dissolved, the sulphate of lead being precipitated, and is obtained by slow evaporation, in regular prismatic crystals *.

The same acid exists, in a similar state of combination, in other species of sorrel; and it is found in other vegetables. The earthy-like matter disseminated in streaks in the root of rhubarb, Scheele found to consist of oxalic acid, combined with lime †; and he found it also in the roots of many other plants, as bistort, liquorice, florentine orrice, squil, turmeric, tormentil, ginger, &c. and in the barks of cannella, cascarilla, cinnamon, quassia, oak, elm, and others ‡. Deyeux found, that the acid juice contained in the fibres of chick pease was pure oxalic acid; though Dispan has since stated some imperfect experiments, in consequence of which he considered the acid obtained from this vegetable to be a peculiar one, to which he gave the name of Ciceric ||.

The artificial formation of this acid from sugar is effected according to the process described by Bergman. One ounce of refined sugar, in powder, is mixed in a tubulated retort, with three ounces of strong nitrous acid, the specific gravity of which is 1.567: when the solution is completed, and the disengagement of nitric oxide gas which attends it has ceased, a receiver is to be luted to

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* Crell's Chemical Journal, vol. i. p. 108.

† Ibid. p. 34. ‡ Ibid. vol. iii. p. 1.

|| Annales de Chimie, tom. xxx. p. 179.

the retort, and the solution gently boiled. When the liquor acquires a dark brown colour, three ounces more of nitrous acid are to be poured on, and the boiling continued until the coloured and smoking acid has entirely disappeared. The liquor in the retort being poured out, on cooling there are formed in it numerous slender crystals, being quadrangular prisms, and which, when collected and dried on bibulous paper, weigh 109 grains. The remaining liquor, boiled again with two ounces of nitrous acid until the red vapours begin to disappear, on cooling affords 43 grains of crystals. And if to the glutinous liquor which remains after this, there be added, at different times, small quantities of nitrous acid, amounting in all to two ounces; on boiling it to dryness a saline mass is formed, brown, glutinous, and deliquescent, which, when perfectly dried, amounts to half a drachm, but in purifying loses nearly half its weight *. The quantity, however, obtained of the acid in this process, is liable to vary; for if the nitric acid be boiled too long, a portion appears to be decomposed, and the crystallized product is of course diminished. The crystals require to be rendered pure by repeated solutions and crystallization.

The changes that are effected in this production of oxalic acid from sugar, are not yet perfectly ascertained. Oxygen is indeed communicated from the nitric acid; but it remains rather uncertain how this operates in the production of the acid. From the small quantity of acid obtained from a given quantity of sugar, it is obvious that it does not merely combine directly with the saccharine

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* Bergman's Essays, vol. i. p. 304.

matter so as to acidify it: it therefore unites with portions probably both of its carbon and hydrogen, forming water and carbonic acid, and leaving the remaining elements in those proportions, and in that state of combination, which constitutes oxalic acid. There is also always a formation of malic acid, and the uncrystallizable residual liquor consists principally of this.

This acid is formed also from other vegetable substances subjected to a similar process. Bergman obtained from 100 parts of gum arabic about 26 of acid; from 8 of alkohol, 3 parts; and from a great number of vegetable products, it may be obtained, as has been already observed, in greater or less quantity. It is even afforded by some animal substances, being left when they have been acted on by nitric acid so as to disengage their nitrogen. The theory of its production in these cases must be the same.

The acid obtained by these different processes, when perfectly freed from foreign matter, is precisely the same. It has been generally examined by chemists in the state in which it is afforded by the oxygenizement of sugar, as this process is less troublesome than extracting it from the salt of sorrel. We are indebted to Bergman for a knowledge of its principal properties and combinations.

Oxalic acid crystallizes in slender four-sided rhomboidal prisms, bevelled at each extremity, subject, however, to various modifications. The crystals are of a white colour, permanent in the air, or slightly efflorescent. Their taste is very sour, and they communicate this, as well as the power of reddening the vegetable colours, to a large quantity of water. Twenty grains give a sensible acidity to three pints. They are soluble in twice their weight of cold water, and in an equal weight of boiling water. They are also soluble in alkohol; 100 parts when boiling, taking up nearly 56 of the acid, at an inferior heat not above 40. They dissolve in sulphuric ether, but with difficulty *.

Exposed to heat, the water of crystallization is first dissipated, and the acid melts: when it begins to boil, it becomes brown, and is decomposed; a quantity of an acid liquor passes over; an acid powder is condensed in the neck of the receiver, which is the oxalic acid, extremely pure, the residuum being a brown or grey matter; and a large quantity of elastic fluid is disengaged during this decomposition, of which about one-half is carbonic acid; the other is inflammable, and appears to be carbonic oxide, or a variety of carburetted hydrogen. About 100 cubic inches of this mixed aërial fluid are obtained from the experiment performed on half an ounce of the crystals, of which, from the account Bergman gives of it, it is evident that only part is decomposed. When the sublimed portion of acid is again subjected to the same operation, it is partly sublimed, and partly resolved into an acid liquor not crystallizable; and by repeating it a third time, the decomposition is completed. In this analysis it is to be remarked, as Fourcroy has stated, that there is no production of empyreumatic oil; which appears to prove, that this acid contains little hydrogen in its composition, but that its chief constituents are carbon and oxygen; and as the other vegetable acids are resolved into it by the action of oxygen, it probably contains a large propor-

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* Bergman's Chemical Essays, vol. i. p. 308. &c.

tion of this principle. According to Fourcroy[*], Vauquelin and he found in their investigations, that it is composed of 77 of oxygen, 13 of carbon, and 10 of hydrogen.

Oxalic acid is decomposed by the more powerful mineral acids. Sulphuric acid renders it brown, and when boiled on it entirely decomposes it. Nitric acid dissolves it, and when heat is applied becomes yellow; on cooling, crystals are again deposited; but if this operation be frequently repeated, the oxalic acid is at length destroyed. Muriatic acid dissolves the crystallized oxalic acid, when assisted by heat, without decomposing it. [*]

Oxalic acid combines with the alkalis and earths, forming salts, named Oxalates, of which some are soluble and crystallizable, but the greater number are of sparing solubility.

Oxalate of potassa, when exactly neutral, is not easily crystallized; but, if there be a slight excess, either of acid or of alkali, crystals are formed without difficulty. It is very soluble; and its solution, on evaporation, becomes gelatinous. When there is an excess of acid, crystals are easily obtained; they are deposited merely by dropping a solution of potassa into a solution of oxalic acid, and, when formed by evaporation, are regular, and nearly of the same form as the acid itself. The native salt of sorrel, it has been already observed, is a super-oxalate of potassa. It occurs generally in small irregular crystals, permanent in the air: its taste is sour, and it reddens immediately the vegetable colours. It is very soluble in water, especially in boiling water, which, according to Wenzel, dissolves two-thirds of its weight. Its solution does not decompose spontaneously as those of almost all the salts containing acids of vegetable origin do. The stronger acids decompose it partially with difficulty: the alkaline, and some of the earthy bases, as barytes and magnesia, enter into combination with its principles, and form triple salts. Lime decomposes it entirely by attracting its acid. It is decomposed by heat; an acid liquor being distilled over, which appears to be oxalic acid with little alteration.

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[*] System, vol. vii. p. 306.

Oxalate of soda is not very soluble, and can scarcely be obtained in regular crystals. It is separated, in its formation by the combination of its principles, in crystalline grains. This salt is also disposed to combine and crystallize with an excess of acid.

Oxalate of ammonia, formed by saturating water of ammonia with oxalic acid, is obtained by slow evaporation in quadrangular prisms, in which there is an excess of acid, and which are soluble in water, but not in alkohol. When exactly neutralized, it appears to be still more soluble.

Oxalate of barytes is deposited in pellucid angular crystals, when oxalic acid is saturated by the addition of barytic water: they are scarcely soluble in water: boiled in distilled water, they split and fall to powder, but, on cooling, the small portion which is dissolved, again forms into similar crystals; the salt, by the agency of the water in this experiment, being apparently converted partly into a sub-oxalate, and partly into a super-oxalate. Oxalate of strontites is likewise insoluble. With lime, in any state of combination, oxalic acid immediately combines, and forms a compound of very sparing solubility, which is precipitated in the state of a powder. According to Bergman's estimate, 100 parts of this salt consist of 48 of acid, 46 of lime, and 6 of water. The compound is not easily decomposed by any single affinity, and, from its insolubility, as well as the force of attraction which its principles mutually exert, lime is the most delicate test to discover the presence of oxalic acid, as this acid is to discover the presence of lime. Oxalate of magnesia appears, when formed by saturating oxalic acid by magnesia, in the form of a white powder, not soluble either in water or in alkohol, and consisting of about 35 of magnesia, and 65 of acid. Oxalate of argil is formed by digesting pure argil in oxalic acid: the solution on evaporation does not yield crystals, but a yellowish pellucid mass, of a sweetish astringent taste, which, when dry, deliquesces in a moist atmosphere: it is sparingly soluble in alkohol. Bergman states the proportions of its constituent parts at 44 of earth, and 56 of acid and water.

Oxalic acid acts on several of the metals, especially those which are capable of decomposing water so as to pass to an oxidized state; it unites with their oxides; and it decomposes a number of the metallic salts. The principal metallic oxalates have been described by Bergman, and a few facts with regard to them have been added by Fourcroy.

On oxide of gold it scarcely exerts any action but blackening it. It dissolves precipitated oxide of platina, and forms a yellow liquid which affords crystals of the same colour. It precipitates oxide of silver from its solution in nitric acid, forming with it a white powder scarcely soluble in water, and still less so in alkohol; soluble in nitric acid, and blackened by the action of the solar rays. When heated in a spoon over burning fuel, it is dispersed with a kind of fulmination. Oxide of mercury is dissolved by the acid, forming a white pulverulent salt, which is not soluble in water unless it has an excess of acid, and which is blackened from exposure to the sun. The same combination is obtained by adding oxalic acid to a solution of nitrate or muriate of mercury. It fulminates sensibly when heated. Copper, even in the metallic state, is dissolved by this acid; and with still more facility when it has been previously oxidized: a powder is formed of a pale blue colour, scarcely soluble in water. A similar compound is precipitated when the acid is added to a solution of any of the salts of copper. Iron is likewise dissolved by it with a disengagement of hydrogen gas: the solution has an astringent sweetness, and, when prepared without heat, exhibits prismatic crystals of a greenish-yellow colour, easily soluble in water, and which retain an excess of acid. The solutions of iron highly oxygenized, are precipitated by the acid in the state of a powder of a fine red colour. Lead digested with oxalic acid is corroded, but scarcely dissolved; but when in the state of an oxide combines with it, and the solution, when approaching to saturation, forms crystalline grains, which subside, and which are scarcely soluble in water, except from an excess of acid being added, and not at all in alkohol: this precipitation happens too when any of the salts of lead is decomposed by the acid. Oxalate of tin is formed by the action of the acid on the metal assisted by heat: the solution has a styptic taste, and exhibits prismatic crystals, or when evaporated quickly to dryness a horn-like mass. Zinc is dissolved by the acid with facility, and with a strong effervescence, from the disengagement of hydrogen gas; a white powder is formed, not soluble in water, unless from an excess of acid. With oxide of bismuth, it forms a white pulverulent salt, scarcely soluble in water; and a similar compound in transparent grains is slowly deposited on the addition of oxalic acid to nitrate of bismuth. Nickel digested with it is covered with a greenish-white crust; and a powder of a similar appearance is precipitated by it from the salts of nickel: this powder is soluble in water in small quantity, and assumes a yellow colour. Cobalt is dissolved by it, or rather is converted into a powder of a pale rose colour, scarcely soluble in water, but becoming soluble from an excess of acid; and a similar compound is formed by the addition of the acid to any of the salts of cobalt. Black oxide of manganese effervesces with oxalic acid, probably from the disengagement of oxygen gas; and the saturated solution deposites a white powder scarcely soluble in water, unless the acid be in excess: this is also formed by the addition of the acid to the solutions of manganese. Antimony in the state of oxide is dissolved slowly: the solution in which the acid is predominant, affords crystalline grains, which are scarcely soluble in water. White oxide of arsenic is easily dissolved; and the solution on evaporation affords prismatic crystals, which, melting with a gentle heat, emit the superabundant acid: they are still soluble in water and alkohol; and are sublimed and decomposed by heat.

Oxalic acid is scarcely applied to any use except as a chemical test. *It has already been stated, that it is one extremely delicate in detecting the presence of lime.* According to Bergman, one grain of the concrete acid of the size of a pin's head, discovers one grain of pure lime in 42.250 grains of water by the cloud it produces. It is rendered less delicate by the presence of any free acid either existing in the liquid containing the lime, or disengaged from a state of combination with the lime itself; and hence such acid ought to be saturated previously by an addition of ammonia, or oxalate of ammonia, instead of pure oxalic acid, should be used. Brugnatelli published some experiments to prove that oxalic acid is a less delicate and less accurate test of lime than is generally supposed; and that this earth is not indicated by it when it is known to exist, or when it is detected by other tests *. Darracq repeated these experiments, and found them incorrect, except in so far as regards the effect of an excess of any acid in preventing the precipitation of oxalate of lime which had been before known to chemists, and which can be obviated by the methods pointed out †.

Super-oxalate of potassa, the native salt of sorrel, is used under the name of Salt of Lemons, to remove ink-stains from linen; an effect it produces by the oxalic acid dissolving with facility the oxide of iron in the ink, on the combination of which with the tannin and gallic acid the colour depends; while, at the same time, it can be used without any risk of injury to the cloth, on which it does not act.

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* Annales de Chimie, tom. xxix. p. 174.

† Ibid. tom. xl. p. 68.

SECT. XIX.

TARTARIC ACID.

A SALINE matter is deposited from wine, during the progress of the slow fermentation it suffers on keeping, which has been long known by the name of Tartar, and, when purified, from the colouring matter which adheres to it, by that of Crystals or Cream of Tartar. It was also known to the chemists, that an alkali, potassa, could be obtained from it, by calcining it with a moderate heat; and it was by this process, indeed, that this alkali was generally obtained for chemical and medicinal use. It was maintained by some of the older chemists, Lefevre, Glazer, and others, that this alkali pre-existed in the salt; and this was more clearly established by the experiments of Duhamel, Margraaf, and Rouelle. The acid which exists in it is in excess, so as to be sufficiently obvious by the sour taste and acid powers of the salt. Scheele gave the process by which it could be extracted, and thus discovered the properties of this acid in its pure state.

Tartar, or super-tartrate of potassa, as it is properly named, is not, as some chemists have imagined, the product of fermentation. The experiments of Boerhaave, Neuman, and other chemists, have proved, that it is contained in the juice of the grape previous to its conversion into wine. It has also been discovered in other fruits, particularly in the tamarind; and it is said to exist in the roots of sage, germander, and some other plants. It ex-

ists in these, however, in small quantity, and it is the deposite from wine that is met with in commerce. It is named Red or White Tartar, according as it is more or less coloured, from part of the colouring matter of the wine adhering to it. Besides this, it is rendered impure by the presence of some other substances, particularly tartrate of lime. It is purified by dissolving it in water, and boiling its solution with a small quantity of fine clay diffused through it. This attracts the colouring and extractive matter, and the solution, on cooling, affords crystals of a white colour. These form the purified tartar, or crystals of tartar of commerce, in which, with the super-tartrate of potassa, there may still exist a small portion of tartrate of lime.

The process which Scheele employed to extract the acid from this salt, consisted in dissolving any quantity of the purified super-tartrate in boiling water, and throwing into it chalk in powder, as long as any effervescence was excited, and until the acid was entirely saturated, as was indicated by the liquid not reddening the vegetable colours. The lime of the chalk combines with the excess of tartaric acid in the super-tartrate; and this tartrate of lime being insoluble, is precipitated, while neutral tartrate of potassa remains in solution. The tartrate of lime, well washed with water, is put into a glass-matrass: a quantity of sulphuric acid equal to that of the chalk employed, and previously diluted with half its weight of water, is added. This is digested in a sand-bath for twelve hours, stirring the mixture occasionally. The sulphuric acid combines with the lime, and forms the sulphate of lime, which is nearly insoluble: the tartaric acid is dissolved *by the water: the solution is poured off, and the remain*ing sulphate of lime is washed with water, which is added to this solution. To ascertain that no sulphuric acid is present, a few drops of acetate of lead are added, which forms a precipitate, soluble in vinegar if the tartaric acid be pure, insoluble if it be contaminated with sulphuric acid. If the latter be the case, it is digested with a little tartrate of lime, and the sulphuric acid is thus abstracted. The solution is then evaporated, and the tartaric acid is obtained in a crystallized form, equal in quantity to about one-third of the super-tartrate that has been employed. Muller has given the proportions to be employed in this process with more precision. They are 6 lbs. of chalk diffused in 36 lbs. of boiling water, and as much super-tartrate of potassa as this quantity of chalk saturates: There are then to be added to the tartrate of lime, diffused in a large quantity of water, 6 lbs. of sulphuric acid, of the specific gravity of 1.817, with which 6 drachms of nitric acid have been mixed *. The sulphuric acid does not appear, in Scheele's process, to be sufficiently diluted, so as to prevent it entirely from acting on the tartaric acid. Lowitz has remarked, that it ought to be diluted with at least four times its weight of water †.

In this process, it is only the excess of tartaric acid contained in the super-tartrate that is obtained; and a quantity of it still remains combined with the potassa, which the chalk is not able to decompose. It has therefore been proposed to employ lime instead of chalk, by

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* Annales de Chimie, tom. vi. p. 38.

† Ibid. vol. xxxiv. p. 180.

which the decomposition is complete, and the whole of the tartaric acid abstracted; but in this case, as Vauquelin has remarked, part of the tartrate of lime is prevented from precipitating by the action of the pure alkali; and it is therefore doubtful if this method is preferable to the process of Scheele.

It has been proposed, too, to obtain this acid by dissolving one pound of super-tartrate of potassa in six pounds of water, and adding a quarter of a pound of concentrated sulphuric acid. But this method is very imperfect, the alkali being merely shared between the two acids, and no pure tartaric acid obtained.

This acid has received its name from the substance from which it is always obtained. It was until lately named the Tartarous Acid; but the propriety is now acknowledged of giving the names of all the vegetable acids the same termination, and hence it is denominated Tartaric Acid.

The form of the crystals of this acid has been very variously described. I have obtained it in thin broad tables,—a form described by Bergman and Fourcroy; but it is also said to occur in prisms and in pyramids. When pure, the crystals are nearly transparent. Their taste is very sour, and a small portion immediately reddens the vegetable colours.

This acid is very soluble in water, so that a concentrated solution can be obtained of nearly an oily consistence. It is not very liable to spontaneous decomposition, especially if the solution is not very largely diluted.

Exposed to heat, it is decomposed: a considerable quantity of an acid liquor is obtained, which was formerly considered as a peculiar acid, and received the name of Pyro-tartarous, but which Fourcroy and Vauquelin have shown to be acetic acid, diluted, and disguised by a small portion of empyreumatic oil *. With this acid, a quantity of oil which separates from it is condensed in the receiver: much aërial fluid, consisting of carbonic acid and carburetted hydrogen, is disengaged, and a bulky coal remains. According to Fourcroy's statement of the result of its analysis by himself and Vauquelin, it consists of 70.5 of oxygen, 19 of carbon, and 10.5 of hydrogen,—a larger proportion of carbon, and less of oxygen, than what enter into the composition of oxalic acid. It is converted, according to the experiments of Hermbstaedt, into this acid, by distilling from it repeatedly six times its weight of nitric acid; 360 parts of the tartaric acid, according to these experiments, yield 560 of crystallized oxalic acid,—a quantity which would prove, if sufficiently established, the fixation of a very large proportion of oxygen †.

This acid combines with the alkalis and earths, forming salts; which, while it had the name of Tartarous acid, were denominated Tartrites, but which are now named Tartrates. It appears to have a peculiar tendency to form triple salts, which crystallize with great regularity, and exhibit marked properties, and some of which are important from the uses to which they are applied.

The neutral tartrate of potassa is not formed by the direct combination of its acid and base, but by saturating the excess of acid in the super-tartrate, by the addition of

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* Annales de Chimie, tom. xxxv. p. 172.

† Fourcroy's System, vol. vii. p. 351.

the requisite proportion of alkali; a quantity of carbonate of potassa being dissolved in boiling water, and super-tartrate of potassa in fine powder being added in small quantities at a time, diffusing it well through the solution by constant stirring, as long as there is any effervescence, and until exact neutralization is attained. The solution is filtered, and as it is not easily crystallized, it is at once evaporated to dryness, when this salt is prepared for medicinal use. Being much more soluble than the super-tartrate, it was formerly named Soluble Tartar.

Though difficult of crystallization, yet when its saturated solution is allowed to stand for some months, large and regular crystals form, which are tetraedral prisms, bevelled at each extremity, and usually aggregated. Its taste is bitter; it is deliquescent in a humid atmosphere, and is very soluble in water, not requiring four times its weight of cold water for its solution. When in solution, it decomposes spontaneously when kept for some time, or rather its acid suffers this change, so that at length its alkali remains in the state of a carbonate. A similar decomposition, as to the ultimate result, is effected by heat. It is very susceptible of decomposition, from the action of other acids, which abstract from it so much of its acid as to reduce it to the state of super-tartrate.

This salt, the super-tartrate of potassa, requires notice as a distinct one, as its composition is determinate, and its properties well marked. Its origin, and the method of purifying it, have been already stated. It occurs in small crystalline masses, the figure of which can scarcely be determined; of a white colour, and semi-transparent; brittle, and easily reduced to powder, and having a sour taste.

This salt requires a considerable quantity of water for its solution; about sixty parts of cold, or thirty of boiling water. This solution decomposes spontaneously when long kept; the principles of the acid entering into new combinations, and leaving the alkali: and by this simple experiment, the older chemists demonstrated, that the alkali pre-exists in this salt, and is not formed by the calcination by which it is usually obtained.

The sparing solubility of this salt, affords us the best test to discover tartaric acid; a solution of potassa, when added, so as to leave an excess of acid, forming a turbid fluid, from which, in a short time, small crystals of the super-tartrate subside. It is also the best test we have to distinguish potassa from soda.

When super-tartrate of potassa is exposed to a strong heat, it is fused, becomes of a black colour, and is decomposed: it gives a large quantity of empyreumatic acetic acid, an oil, with carbonic acid, and carburetted hydrogen gases, the alkali remaining in the state of carbonate, mixed with charcoal. A quantity of carbonate of ammonia is also said to sublime: from which it might be inferred, that nitrogen enters into the composition of the acid: but the fact is not well ascertained, and a small quantity produced might arise from foreign matter contained in the salt. This process of decomposing this salt by heat, was that formerly employed by chemists to obtain carbonate of potassa: it was performed in a crucible, and the residual matter was lixiviated with water, and then evaporated: and it has been supposed, that it affords the alkali purer than as it is procured by other processes.

From the tendency of tartaric acid to form ternary combinations, this salt exerts peculiar actions on a number of substances. Thus it unites both with soda and ammonia, and with each forms ternary compounds. Thenard has found, that it may even admit the combination of certain proportions of lime, barytes, or strontites; for although when large quantities of these earths are brought to act upon it, they decompose it and abstract the tartaric acid, yet when they are added in a state of solution in small quantity, they occasion no decomposition, but enter into combination with its principles; the liquid remains transparent, up nearly to the point at which the acid of the super-tartrate is saturated, by the earth added; and if this point be not exceeded, there will be formed on the sides of the vessel, transparent crystals, in which analysis detects the presence of the acid, the alkali, and the earth that has been added. Magnesia and argil likewise enter into similar combinations, but form compounds which are not crystallizable *. A singular effect produced on it by borax, or even by pure boracic acid, is, that of increasing greatly its solubility in water, or rather forming with it a very soluble compound: one part of boracic acid, according to Lassone, with four parts of the super-tartrate, being soluble in six or eight times its weight of water. It acts too on several of the metals, and forms triple combinations, some of which have been used in medicine.

According to Thenard's estimate of the composition of super-tartrate of potassa, it consists of 57 of acid, 33 of alkali, and 7 of water.

Tartrate of soda crystallizes in fine needles, or in thin plates: it is soluble in water, but if combined with an excess of acid its solubility is diminished.

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* Nicholson's Journal, 4to, vol. v. p. 268.

A triple salt, the Tartrate of potassa and soda, has been long used in medicine, and known under the name of Rochelle Salt. It is prepared by saturating the excess of acid in the super-tartrate of potassa, by the addition of the requisite quantity of carbonate of soda; a small quantity of tartrate of lime, derived from the tartar, is generally precipitated in consequence of the saturation; the liquor is strained, and, on evaporation and cooling, affords very regular crystals, rhomboidal six or eight sided prisms, hard and transparent. They are permanent in the air, soluble in about five parts of cold water, and in less warm water, and consist, according to the manner in which Vauquelin has stated their composition, of 54 parts of tartrate of potassa, and 46 of tartrate of soda.

Tartrate of ammonia is a very soluble salt, which however crystallizes in slender prisms. The tartrate of potassa and ammonia, formed by saturating the excess of acid in the super-tartrate of potassa by ammonia, forms a salt, soluble, and which crystallizes very regularly in hexaedral prisms accuminated by six planes.

The binary combinations of this acid with barytes and lime are insoluble in water, but may be dissolved by an excess of acid. Those of magnesia and argil, though soluble, are not crystallizable, their solutions forming, on evaporation, viscid or gelatinous masses. The ternary compounds which these form, when potassa enters into the combination, have already been noticed.

Tartaric acid is capable of acting on the metals, at least on those which are capable of decomposing water, so as to be oxidized; and it readily combines with the oxides of the others. Few of these combinations, however, have been examined, or are of importance. The acid does not precipitate the solutions of gold, platina, or silver; but its salts do, from the exertion of a double affinity. In the same way it may be combined with oxide of mercury, and forms an insoluble compound. It unites with oxide of copper, and forms a compound of little solubility, of a green colour. It acts on iron in its metallic state, and dissolves it with effervescence; the solution, on evaporation, does not crystallize, but becomes gelatinous. On zinc its action is similar. It combines with the oxides of tin and lead, decomposing their solutions, and forming compounds of a white colour. In the same manner it precipitates the solution of bismuth of a fine white colour, forming what has been known under the name of pearl white. It dissolves the oxides of antimony, forming a compound which crystallizes irregularly and with difficulty.

Ternary combinations can also be easily formed, by subjecting metals or their oxides to the action of super-tartrate of potassa. Thenard has examined several of these *; and one of them, that with oxide of antimony, has been long an object of attention to chemists, from its extensive medicinal use.

According to Thenard, the alkaline tartrates (as he names these compounds) of manganese, iron, zinc, and tin, are very soluble, and are of difficult crystallization: they are not decomposed, either by the pure alkalis or the alkaline carbonates, but are decomposed by sulphuretted hydrogen, the hydro-sulphurets, and the gallic acid. The

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* Nicholson's Journal, 4to, vol. v. p. 269.

alkaline tartrates of silver and of mercury suffer decomposition, however, not only from these agents, but likewise from the alkalis, either pure or in the state of carbonate. The alkaline tartrate of lead is not soluble; that of copper is distinguished by its saccharine taste, and the great quantity of metal which it contains. The tartrate of potassa and antimony is by far the most important of these combinations: it is the substance which has been long used in medicine under the name of Emetic Tartar, and which is superior to all the other antimonial preparations, in the certainty and uniformity of its operation. The method of preparing it and its properties, have already been taken notice of under the history of antimony.

Tartaric acid, in its pure state, is not applied to any use; and of its combinations, some only are employed in the practice of medicine.

SECT. XX.

BENZOIC ACID.

It has been remarked, in treating of the balsams, that they all contain a peculiar acid, which is obtained from them by the application of heat. The concrete balsam, named Benzoin, being that from which it is usually procured, ithas received the name of Benzoic Acid.

The common process for obtaining it is extremely simple. A quantity of benzoin being reduced to coarse powder, is put into an earthen pot or matrass, to the mouth of which a large paper cone is adapted; a moderate heat is applied; the benzoin melts, and at the same time the acid is volatilized in white vapours: these condense, and adhere to the sides of the cone in small brilliant crystals, which, when the sublimation is slow, appear in the form of long slender prisms. The paper cone is changed as it becomes warm, a new one is applied, care being taken through the whole operation not to raise the heat too high, as then a quantity of oily matter is volatilized, by which the acid is coloured brown. If the heat be applied as long as any product is volatilized, a larger quantity of benzoic acid is obtained than by any other process: Chaptal recommended this method, purifying the acid by repeated solution and crystallization; but it is difficult to separate the oily matter from it entirely.

Geoffroy long ago discovered that this acid might also be extracted from benzoin by the action of boiling water; the water, after having been boiled on the benzoin in powder for some time, being filtrated, affords crystals of the acid on cooling.

Scheele proposed another method of obtaining it in the humid way more economical. Four parts of benzoin in powder and one part of slaked lime are mixed with 24 parts of water, and boiled with it for half an hour. The benzoic acid combines with the lime, and forms a compound soluble in water. The undissolved matter is allowed to subside, and the liquor when clear is poured off: a fresh quantity of water is boiled on the residuum, and the ley thus obtained is added to the former; and this is repeated for a third time. The whole is to be reduced by evaporation, and to the concentrated solution there is to be added gradually muriatic acid, until it be sensibly acid; the muriatic acid combines with the lime, and the muriate of lime is dissolved by the water; the benzoic acid being insoluble in cold water is precipitated in a powder of a brownish colour: this is washed with a little water, is then dissolved in boiling water, the solution is filtered, and as it cools colourless crystals of benzoic acid form. About 14 drachms are obtained by this process from one pound of benzoin. Gren introduced a slight modification of it, by boiling the benzoin with carbonate of soda, and adding to the filtered liquor diluted sulphuric acid, so as to precipitate the acid of benzoin; the only advantage of this is, that it is supposed to be more economical, from the sulphuric being less expensive than the muriatic acid.

Mr Brande has given the following as the quantities of benzoic acid, obtained by these processes, from one pound of benzoin.

	oz.	dr.	scr.	gr.
By Scheele's,	1	6	2	19
— Chaptal's,	2	0	0	0
— Geoffroy's,	1	0	0	10
— Gren's,	1	5	1	10 [*]

It has already been observed, under the history of the balsams, that there is every reason to conclude, that in these processes the benzoic acid is not actually formed, as some chemists have imagined, but is merely extracted.

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[*] Nicholson's Journal, vol. x. p. 88.

A fact observed by Mr Hatchet with regard to its production, might favour, however, the former opinion, or at least lead to the conclusion, that the quantity of acid is increased by a new formation of it. He found, that the balsams, when they had been mixed with sulphuric acid, afforded a considerable quantity of benzoic acid by sublimation, and that some even, as dragons' blood, afforded it when subjected to this treatment, which did not afford it when exposed to heat alone *. But it is not improbable that the acid may merely facilitate its separation, by the action it exerts on the resinous matter, and perhaps by preventing the formation of empyreumatic oil, so as to allow of the heat being raised higher or applied for a longer time.

Benzoic acid is likewise formed in the animal system. It is found particularly in the urine of the horse, cow, and other gramenivrous animals. Fourcroy appears to suppose, however, that it is derived from some of the grasses on which these animals feed. It is also sometimes found in the urine of children, and in general is more or less present when phosphoric acid is deficient.

Benzoic acid is, according to the method in which it has been obtained, in soft-like flakes, or in slender needle-like crystals, frequently of considerable length; when pure, white and brilliant. Its taste is pungent, and slightly acidulous. It has a peculiar odour, somewhat aromatic, and which becomes strong when it is heated and volatilized. This was considered as essential to it; but, from the experiments of Giesse, it appears to be not so,

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* Philosophical Transactions, 1805.

benzoic acid having been obtained by him perfectly inodorous, without any of its other qualities being changed. This he effected by combining the acid with a solution of potassa, and precipitating it from this combination by muriatic acid. On each repetition of this experiment, the odour diminished, and, after the third, it had entirely disappeared. Another process, more simple, and equally successful, was to dissolve the odorous acid in as small a quantity as possible of alkohol: to drop into the solution water until the acid was precipitated: this acid, when dried by a gentle heat, was found to be inodorous; the small quantity of oily matter derived from the balsam to which its odour is owing remaining combined with the alkohol *.

This acid is volatilized by heat, as is evident from the manner in which it is prepared, and its vapour is acrid and suffocating: it is also fusible; and when it has become solid after fusion, its surface exhibits a stellular radiated appearance. Heated on burning fuel, it inflames. Urged with a strong fire in close vessels, the portion that is not immediately sublimed is decomposed, and affords an acid liquid, a quantity of oil more abundant than what is produced in the decomposition of any other vegetable acid: carburetted hydrogen is also disengaged in a considerable proportion, and a small quantity of charcoal is left in the retort. This decomposition is more completely effected when the volatilization of the acid is prevented by previously mixing it with sand. The results show, that it is composed of the usual principles of vegetable matter,

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* Philosophical Magazine, vol. xiv. p. 331.

and, compared with the other vegetable acids, that hydrogen predominates in its composition, to which, probably, its volatility and inflammability are owing.

It is scarcely soluble in cold water. According to Wenzel and Lichtenstein, 400 parts of cold water are required for dissolving one part of it; while the same quantity of boiling water can dissolve 20 parts of it, 19 of which again separate by crystallization on cooling. Its hot solution reddens the infusion of litmus.. Alkohol dissolves it abundantly; and it is precipitated from this solution by the addition of cold water.

Benzoic acid is not easily decomposed by the mineral acids. Sulphuric acid dissolves it; and, on the addition of water, the benzoic acid is again separated unaltered, a small portion of it having been decomposed, as, according to Bergman, a little sulphurous acid is formed. Nitric acid likewise dissolves it, and water equally separates it from this solution unaltered; but if the acid be distilled from it, it suffers, according to Hermbstaedt, some chemical change.

This acid unites easily with the alkalis and earths. Its salts are denominated Benzoates: their properties are not important, and have not been very fully described.

Benzoate of potassa is obtained in acicular crystals, which are soluble in water, and deliquescent. Benzoate of soda is equally scluble and crystallizable, but, according to Bergman, does not deliquesce. Benzoate of ammonia is possessed of the same properties; is volatile, and easily decomposed. Benzoate of barytes, unlike many of the barytic salts, is likewise very soluble, and crystallizes without difficulty. The same may be said of benzoate of lime. The benzoates of magnesia and argil are soluble, crystallizable, and deliquescent.

The combinations of benzoic acid with the metals have been made the subject of experiment by Trommsdorff. He boiled, either on the metal in a state of mechanical division, or on its oxide, the acid of benzoin, with as much water as was sufficient for its solution; and by this general experiment established the following results: With oxide of gold, a solution was obtained which shoots into irregular crystals, which are permanent in the air, dissolve with difficulty in water, and scarcely at all in alkohol. The oxide of silver is scarcely dissolved; but a benzoate of this metal is obtained, by adding benzoate of potassa to a solution of nitrate of silver: a precipitate is thrown down, which is soluble in hot water, but precipitates again on cooling, and which, like the other salts of silver, is blackened by light. The solution of oxide of platina affords minute aggregated crystals, permanent in the air, difficultly soluble in water, and insoluble in alkohol. The solution of oxide of quicksilver affords by evaporation a white brilliant mass, somewhat soluble in alkohol, but not sensibly soluble in water. Oxide of copper is easily dissolved by the acid, and a solution obtained, which shoots into small pointed crystals of a dark green colour, difficultly soluble in water, and insoluble in alkohol. Oxide of tin is not dissolved. Lead is somewhat eroded, and its oxide is dissolved readily, forming a solution of a sweetish taste, which shoots into very white shining crystals, soluble both in water and in alkohol. Iron is dissolved in small quantity: the solution obtained from the oxide affords crystals of a yellowish tinge, having a sweet taste, which are soluble in water, and become more highly oxidized from exposure to the air. The solution of oxide of zinc has a sweet styptic taste, and yields arborescent crystals, which are soluble both in alkohol and water. The solution of oxide of bismuth yields a light mass, composed of white crystalline spiculæ, easily soluble in boiling water, and sparingly soluble in alkohol. Oxide of antimony affords a solution which does not crystallize, but, on evaporation, gives a white flaky mass, readily soluble in water and in alkohol. White oxide of manganese is dissolved by the acid boiled on it, and, by evaporation, small scaly crystals are obtained, abundantly soluble. Oxide of nickel gives a solution of a pale green colour, which does not crystallize. The solution of oxide of cobalt affords crystals of nearly the same figure as the benzoic acid itself. The solution of oxide of arsenic gives plumose crystals, which exposed to the air effloresce, which are dissolved easily in hot water, and crystallize on cooling *.

Benzoic acid, either in its pure form, or in any of its combinations, is applied to no use. It was formerly employed in the practice of medicine, and still enters into one or two officinal preparations; but it does not appear to have any medicinal virtue.

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* Crell's Chemical Journal, vol. iii. p. 11.

SECT. XXI.

ACETIC ACID.

THIS, like several of the other vegetable acids, is a native production, and is also capable of being artificially formed. It exists, as has already been remarked, (page 25.) very generally in the sap of vegetables, combined with potassa and lime, and is sometimes also present in excess. It is discovered by evaporating the sap, and adding to the solid matter sulphuric acid: the vapours of acetic acid are then perceived by their smell. It is more peculiarly, however, the produce of fermentation; and the production of it even characterizes one stage of that process. It is under it, therefore, that its chemical history will best be placed.

SECT. XXII.

MOROXYLIC ACID.

THIS name has been given by Klaproth to an acid which he extracted from a saline efflorescence, found by Mr Thompson to form on the trunk of the white mulberry (Morus alba), in the botanical garden at Palermo. The examination of it was imperfect, from the smallness of the quantity of the substance affording it in the possession of Klaproth; but as he regards it as a peculiar acid, it is necessary to give it a place, though farther investigation may perhaps connect it with one or other of the acids already known. In its properties it approaches nearest to the succinic acid.

The saline exudation, according to Klaproth's experiments, consists of this acid in combination with lime, and mixed with a portion of extractive matter. It is of a brown colour; approaches to succinic acid in its taste; swells up when placed on burning fuel, and emits an acrid vapour, leaving an earthy residuum. By solution in water, and crystallization, the saline matter is obtained more pure, and of a lighter colour. The alkaline carbonates precipitate lime from its solution, and precipitates are also formed from it by nitrate of silver and acetite of lead. Exposed to heat, it gives an acid liquor, an empyreumatic oil, the gases that are usually disengaged from vegetable matter; and leaves a residuum of charcoal and lime.

The pure acid was obtained from this salt by two processes. In the first, to a solution of the salt a solution of acetate of lead was added: the precipitate thus formed, and which consisted of the acid united with oxide of lead, was mixed with sulphuric acid, diluted with three times its weight of water. Sulphate of lead was formed, and the filtered liquor, by evaporation, afforded the moroxylic acid, in fine needles of a pale straw colour. In the second, the salt itself was at once decomposed by sulphuric acid, the sulphate of lime separated, and the pure acid obtained.

This acid approaches still more nearly than the salt from which it is obtained to succinic acid in its taste. It remains dry on exposure to the air, and is easily soluble both in water and in alkohol. When heated in a retort, a small quantity of acid liquor is first obtained: a concrete salt next rises, which adheres to the neck of the retort in the form of prismatic crystals, colourless and transparent; a little charcoal remained in the retort. To separate the sublimed salt from the coaly residuum, the whole contents of the retort were dissolved, and the liquor filtered. The solution was perfectly clear, and, by spontaneous evaporation, deposited the acid in colourless crystals. It appears, therefore, that sublimation is the best mode of obtaining it free from the extractive matter, which adheres too strongly to it to be separated in the humid way. This acid, in its pure state, did not precipitate the metallic solutions, as the native salt does from which it is extracted *.

SECT. XXIII.

WOOD OR LIGNIN.

Wood is in every vegetable the basis to which the other principles are attached, or through which they are diffused; the skeleton as it were of the entire plant, and the substance of which its vessels are formed. The bark, and the fibrous part of the leaves, appear to be of a simi-

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* Nicholson's Journal, vol. x. p. 129.

lar nature. The term Woody Fibre has been applied to denote it, or the name Lignin may be given to it as a peculiar principle. It has every claim to be regarded as such, since it is possessed of peculiar properties sufficiently appropriate, and which are possessed by it uniformly as it exists in different plants.

Wood is distinctly fibrous in its texture, and, as forming the solid parts of plants, these fibres are interlaced. It is inodorous, insipid, and perhaps when perfectly pure is free from colour. Its specific gravity is generally inferior to that of water. The wood of plants, however, is frequently possessed of colour, taste, and smell, from the presence of extractive matter, mucilage, resin, or essential oil. It is only when these have been completely extracted by the joint action of water and alkohol, that the wood can, as a chemical principle, be regarded as pure. A fibrous matter often pulverulent, remains after this operation, and it is from this that the characters of this principle must be derived.

The pure ligneous fibre is altogether insoluble in water: even when the water is boiled on it, it is not dissolved. It is equally insoluble in alkohol: and hence it forms the residuum, when any of the solid parts of plants have been acted on by these fluids.

From exposure to the air in a dry state, it does not appear to suffer any change; but when humid, it is gradually decomposed, and passes at length through various intermediate states to that of a black mould, consisting principally of carbon. Saussure *junior* has found, that the oxygen of the atmospheric air is, during this change, consumed, and that it is replaced by an equal volume of carbonic acid gas; and he concludes from his experiments, that the oxygen abstracts part of the carbon of the wood, but that it loses at the same time a larger proportion of its oxygen and hydrogen, which form water; and that by the abstraction of these principles, the proportion of carbon is increased in the residual matter. When the air is excluded, and the wood is decomposed by the influence of water alone, without the contact of oxygen, the changes are different, and the proportion of carbon is rather diminished than increased *. It is known too, that when the air is entirely excluded, wood decomposes with extreme slowness, even though humid, as, for example, when it is buried in the earth. It is only by the joint action of air and water, that its rapid decomposition is occasioned.

According to the same chemist, water boiled on wood, not merely dissolves the extractive matter it contains, but actually forms a portion of it, so that it is impossible to reduce wood by repeated decoctions to such a state that it shall not afford it; each decoction or maceration, with the contact of the air, producing a portion of extract which either did not before exist, or which is rendered soluble by a change in its principles. He boiled a quantity of oak saw-dust, (three ounces), in twenty-four times its weight of water, poured off the decoction, evaporated it so as to ascertain the quantity of matter dissolved, and repeated this a number of times. The quantity of matter afforded by the first decoction was 90 grains; that by the second 29 grains. It continued to diminish to the ninth

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* Recherches Chimiques, p. 148.

decoction; the eleventh and twelfth afforded the same quantity as the ninth, amounting to 4 grains. The remaining saw-dust was then exposed to the air for two months. On being submitted to a new decoction, it gave $5\frac{1}{2}$ grains of extract, a quantity therefore greater than at the ninth decoction: the fourteenth decoction afforded 4 grains: and after a new exposure for two months to the air, the quantity was again augmented to $5\frac{1}{2}$ grains. Wood, the most completely freed of its soluble principles, furnishes always by maceration in water with the contact of air, infusions holding extractive matter dissolved *.

The alkalis act on wood: when an alkaline solution is allowed to remain over any wood, it receives colour, and the colour of the wood at the same time is darkened. With the assistance of heat, they soften, and partly dissolve and decompose it.

The stronger acids also act on it. Sulphuric acid immediately chars it, rendering it in a very short time perfectly black and soft. Nitric acid immediately gives it a yellow tinge; and when acting on it in large quantity, it disengages, according to Fourcroy, a portion of nitrogen gas, and converts it principally into oxalic acid, with small quantities of malic and acetic acids.

When wood is exposed to heat in close vessels, as in an iron retort, a portion of water distils over, which, as the distillation proceeds, becomes more and more acid, and at length a liquor very acid and pungent, of a yellow colour, is condensed; an empyreumatic oil likewise passes over in considerable quantity: carburetted hydrogen,

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* Recherches Chimiques, p. 150.

and carbonic acid gases are likewise disengaged, and a portion of ammonia is produced, which exists neutralized in the acid liquor. A concrete charcoal remains, which retains completely the figure, and even in some measure the texture of the wood. The acid procured in this process, was formerly regarded as a peculiar one, and named Pyro-ligneous Acid. The researches of Fourcroy and Vauquelin have shewn, that it is merely diluted acetic acid, with an impregnation of empyreumatic oil. It is afforded in so large a quantity, that the process is even employed to furnish this acid, for some of the purposes to which it is applied.

When wood is heated, without the air being perfectly excluded, it becomes black, exhales acrid penetrating vapours, composed of the empyreumatic acid and oil, and the charcoal remains. It affords, after its combustion, a quantity of saline matter, principally carbonate and sulphate of potassa and of lime, muriate of potassa, and phosphates of magnesia and lime; and also portions of earths and metals, particularly silex, iron, and manganese. All of these, however, are not essential to the composition; on the contrary, the greater number are rather accidental, and, as Saussure has shewn, often dependent on the soil, and derived from it, as has been already fully stated (p. 103). The portion of charcoal afforded by different woods, is different, being of course more as the wood is compact and dense: and the quantity of saline matter afforded is also different, as has been already remarked, vol. ii. p. 80. On this subject, the researches of Saussure have been extensive; and his tables, which are too numerous to be inserted, present a number of facts on the incineration of different woods, the quantity of saline matter it affords, and the circumstances by which the production of this appears to be influenced.

When the air is freely admitted, and the heat raised to ignition, wood burns. Its combustion is at first vivid, or gives much light, from the extrication of the hydrogen in combination with a part of its carbon; but as this is dissipated, the light is diminished, and there is at length only the red glow of the charcoal. The products of the combustion have not been ascertained with much accuracy. They are principally carbonic acid and water; and if nitrogen be a constituent principle of wood, as its analysis by heat appears to prove, ammonia will probably also be evolved. An ammoniacal salt is accordingly always found in the soot of fuel.

From the analysis of wood, it appears to consist of carbon, hydrogen, oxygen, and nitrogen, with probably lime. It is evidently, of all the vegetable principles, that which contains the largest proportion of carbon; since, independent of the quantity of this principle disengaged in its analysis, in the state of carbonic acid and other elastic products, the residual charcoal amounts to one fourth or fifth of the weight of the original wood. From this predominance of carbon, it probably derives its solidity, and its inactivity as a chemical substance.

CORK is a substance analogous to wood. The substance to which this name is usually appropriated, is the external bark of the Quercus suber; but Fourcroy supposes, that the epidermis of all ligneous vegetables is of a similar nature, and they are probably all varieties of the matter which constitutes the ligneous fibre.

Cork is light, soft, spongy, and elastic: it is inflammable; affords a little ammonia by distillation; and is acted on by chemical agents, in very nearly the same manner as wood.

The principal peculiarity with regard to it, and in which it differs from wood, is that of affording an acid different from every other, when acted on by the nitric acid. This was first observed by Brugnatelli; but the production and properties of this acid, named the Suberic, have been more fully investigated by Bouillon Lagrange *.

The process which he employed to obtain it, consists in pouring on cork in a retort, six times its weight of diluted nitric acid, and distilling it from it with a gentle heat. When the heat is applied, red vapours are extricated; the cork swells and becomes yellow; and as the distillation proceeds, a soft spongy matter rises to the surface. The distillation is continued, until the production of red vapours ceases: the whole, while warm, is poured into a glass or porcelain bason, placed on a sand-bath, and a moderate heat is applied, stirring the matter constantly with a glass spatula. It is thus gradually thickened: and as soon as it ceases to disengage white irritating vapours, the vessel is removed from the sand-bath, and the residual mass agitated until it is nearly cold. A substance is thus obtained, of the consistence of honey, of a yellow colour, and a sharp penetrating odour when

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* Annales de Chimie, tom. xxiii. p. 42.

it is warm, an aromatic odour when cold. To obtain the acid which is contained in it, it is put into a matrass, and twice its weight of distilled water is poured upon it; it is heated so as to liquefy it, and the solution is filtered from the part that is not dissolved by the water. It is of a clear amber colour, and has a smell approaching to that of prussic acid: on cooling it becomes turbid: the precipitate which falls down is separated by filtration, and the acid obtained more pure. It is still, however, somewhat coloured, but the colour is removed, either by saturating it with an alkali, and again precipitating it by an acid, or by boiling it with charcoal. It is obvious, that in this operation the production of the acid is owing to the communication of oxygen from the nitric acid to the principles of the cork, though how far any of these is expended in the formation of products different from the acid, is not determined. Carbonic acid gas is disengaged during the operation, along with the nitrous vapours. The matter deposited during the formation of the acid, consists principally of a substance which separates and assumes the consistence of wax, and of a white tasteless powder, which has some analogy with fecula.

Suberic acid may be obtained in a solid form, but is not crystallizable: it is either pulverulent when it has been precipitated, or when obtained by evaporation is in thin irregular pellicles. Its taste is slightly bitter and acid: dissolved in a small quantity of boiling water, it is irritating to the throat, and excites coughing. It reddens the vegetable colours, and it attracts a little humidity from the air, especially when it is not perfectly pure. Exposed to heat, it is volatilized, and forms crystalline flakes on the sides of the vessel. Heated by the blowpipe, it first liquefies, then becomes pulverulent, and lastly is sublimed, exhaling an odour of sebacic acid. It becomes brown from exposure to light.

At the temperature of 60°, an ounce of water dissolves 10 grains of the concrete acid, but if it is very pure, not more than 4 grains. Boiling water dissolves half its weight.

It is not altered by oxygen gas. The mineral, or the other vegetable acids, have little action on it, and do not completely dissolve it, especially when it is not quite pure. Alkohol developes in it an aromatic odour.

Suberic acid unites easily with the alkalis and earths. Its salts are named Suberates. The mineral acids in general precipitate the suberic acid from their solutions; and they are decomposed by solutions of almost all the metallic salts.

Suberate of potassa, formed by adding suberic acid to carbonate of potassa, crystallizes in four-sided prisms; has a bitter saline taste; is fused and decomposed by heat; and very soluble in water. Suberate of soda does not crystallize: its taste is slightly bitter; it is very soluble in water, and attracts humidity from the air. It is also soluble in alkohol. Suberate of ammonia has a saline bitterish taste: it is crystallizable; is very soluble in water; attracts a little humidity from the air, and is volatilized when heated before the blow-pipe. Suberate of barytes is not crystallizable, and is scarcely soluble in water, except from excess of acid. Suberate of lime is also very sparingly soluble in water: boiling water dissolves a portion of it, but the greater part precipitates on cooling;

nor does it crystallize : it is perfectly white ; its taste is a little saline. Suberate of magnesia is in the form of a powder : it has a bitter taste ; attracts a little humidity from the air ; is soluble in water, and is decomposed by heat. Suberate of argil cannot be obtained in a crystalline form, but, when reduced to dryness by evaporation, is in the state of a dry mass, of a yellow colour, transparent, having a stýptic bitterish taste : if too much heat has been applied, it melts and becomes black.

Suberic acid has no action on platina, gold, or nickel ; but it forms salts with the greater number of the other metals. In general these salts do not crystallize, and they have a tendency to form with an excess of acid. Its action on some metallic solutions give some appearances which m[illegible] serve to distinguish it. It decomposes acetite and nitrate of lead, and nitrates of mercury and silver : with nitrate of copper it forms no precipitate, but the blue colour of the solution passes to green, as does also that of sulphate of copper : the solution of sulphate of iron becomes of a deep yellow, and that of sulphate of zinc of a clear golden yellow.

A character peculiar to it is, that when a few drops of it are added to a solution of indigo in sulphuric acid, it causes the blue colour to pass to a green.

Bouillon Lagrange, in concluding his memoir on this acid, points out the characters by which it is distinguished from the known vegetable acids :—from the citric, by not crystallizing ; from the gallic, by not precipitating iron black ; from the mallic, by being obtained in a concrete form ; from the tartaric, by its volatility ; from the oxalic, by not precipitating the solution of sulphate of copper, and by yielding to it lime. From these, and the various phenomena presented in its combinations, he considers it as proved to be different from all the other acids.

These observations are so far just. Yet it is to be observed, that this acid does not appear to have ever been obtained pure. A portion of extractive matter is formed along with it, in the oxygenizement of the cork, which still adheres to it, and which appears to be only partially abstracted, as is evident from the aromatic odour which alkohol developes in it, and from a fact incidentally mentioned by Lagrange, that it is only by presenting it to carbonate of potassa, that the suberate of that alkali can be formed, as if pure potassa be employed, it acts upon the acid, and gives it a very deep colour. It is obvious, that we cannot determine how far the peculiar properties it exhibits may be owing to the foreign matter thus combined with it.

THE Ligneous Fibre is probably the basis of other vegetable production, as of the fibres of flax, of cotton, and of other vegetables which are dressed and wove into cloth. They agree with it, not only in their natural production and in their texture, but in chemical qualities; particularly in inflammability, insolubility in water or alkohol, and in the changes they suffer from the alkalis, the mineral acids, and other re-agents. And any differences they do present, are probably to be ascribed to their state of aggregation, or to very slight modifications of composition. If this view be just, the basis of Paper must consist also of the same principle, and it exhibits nearly the same chemical qualities.

SECT. XXIV.

AROMA. ACRID PRINCIPLE. BITTER PRINCIPLE. NARCOTIC PRINCIPLE. COLOURING MATTER.

I PLACE these principles under one section, and at the close of the history of the vegetable substances, as their existence, though maintained by some modern chemists, appears to me to be extremely doubtful. The sensible qualities which are ascribed to them, and from which their names and distinctive characters are derived, are such as may belong to any of the known vegetable principles, and are indeed possessed by principles of the most opposite kind; and it appears a very unfounded and unphilosophical hypothesis to assume, that there are distinct principles in which they reside. Should a principle different from others previously known be discovered, which possessed bitterness, or any other of these qualities, and should even this principle be detected in more than one vegetable endowed with the same property, still it ought not to be characterized from it, since it cannot be pretended that that quality is in all cases attached to a principle of this kind, and, as existing in any vegetable product, depends on the presence of a portion of this principle. The principle, therefore, were its existence established, should be distinguished from chemical qualities which belong to it; and the sensible quality, from which in this mode of classification it has derived its name, ought to be considered as rather accidentally than essentially connected with it. As these principles, however, have been supposed to exist, and as with regard to some of them there are some facts which to a certain extent favour the opinion, it may be necessary, in concluding the history of the vegetable proximate principles, to state briefly the observations or the reasonings which have been connected with this subject.

AROMA. This has been considered as the principle in which the odour of vegetables resides. The essential oils of plants very generally possess their flavour; but it was observed, that many vegetables which smell strongly yield little or no essential oil; and the oil, when it is obtained, has not that strong odour we should expect, did the odour of the plant entirely depend on it. This is the case with the violet, jessamine, and many other odoriferous flowers. It was farther observed, that if such vegetables be placed in water, and exposed to a very gentle heat, not sufficient to volatilize their essential oil, they are deprived of their smell, which is in some measure transferred to the water, when the operation is performed in close vessels. The essential oils, too, it was remarked, always lose a great part of their odour from exposure to the air, though little of the oil itself is dissipated. And, lastly, it has sometimes happened, that the atmosphere around odoriferous plants has not only had their odour diffused through it, but received such an impregnation of some inflammable elastic fluid, as to have kindled on the approach of an ignited body. From such facts it was inferred, by some of the older chemists, that there exists in vegetables a subtle principle in which their odour resides; that this is capable of being combined with their other principles, and in particular with their essential oils, to which of course it communicates the odour of the plant. By Boerhaave this principle was named the Spiritus Rector of vegetables; and in framing the modern nomenclature, it received the denomination of Aroma.

The observations of Fourcroy on this subject * are perfectly just. The faculty of exciting the sensation of odour, is a quality which may belong to any kind of matter, and which does belong to many substances, as ammonia, sulphur, and its combinations, the metals, and many chemical compounds, in which we cannot suppose the existence of any common subtle principle on which it depends. And there is no reason to suppose but what it may exist in vegetable products, without being attached to such a principle in them. If its existence were supposed too, numerous species of it must be admitted; for the odour it communicates is its only characteristic property, and this odour is different in every plant: and all the facts from which the existence of it has been inferred, admit of explanation, on the supposition that the odour resides in the essential oil, which is sufficiently volatile to be dissipated at a very moderate temperature, which may be diffused in atmospheric air, or dissolved by it, and which, suffer-

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* Annales de Chimie, tom. xxvi. p. 232.

ing chemical changes from long exposure to the atmosphere, is thus deprived of much of its odour. At the same time, the odour may sometimes reside in some other proximate principles; and indeed the greater number of these may be distinguished by a smell in general faint, but sufficiently perceptible.

ACRID PRINCIPLE. The existence of such a principle has been inferred from a few facts with regard to certain acrid plants. It has been found, that several vegetables which are inodorous, or have only a weak smell, are in their recent state extremely acrid to the taste, and display this acrimony in the irritation and inflammation which they occasion when applied to the skin. Such are the roots of the Scilla maritima, of the Colchicum autumnale, Bryonia alba, and Arum maculatum, and the leaves of the Anemone nemorosa, and of the Clematis erecta. Yet they lose entirely this peculiar acrimony on being dried, while their other active powers frequently remain. From this circumstance, and from their want of odour, it is concluded that the acrimony cannot be supposed to depend on an essential oil. From some of these plants too, this principle is communicated to water or alkohol by distillation from them, though no other property but the acrimony is thus conveyed. There appears some reason, from these facts, to admit the conclusion that has been drawn from them *, that there exists a peculiar vo-

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* Gren, Principles of Chemistry, vol. i. p. 20. Hermbstaedt, Medical and Physical Journal, vol. i.

latile principle in these plants different from an essential oil, in which their acrimony resides. If its existence shall be considered as probable, however, it has never been obtained in such a state as to be submitted to chemical examination, and all that relates to it is therefore uncertain and obscure.

NARCOTIC PRINCIPLE. The existence of such a principle has been inferred from facts somewhat similar to those on which that of an acrid principle has been supposed to be established. It has been found, that many narcotic plants suffer a diminution in their power from age, and that they are also rendered inert by decoction in water, though when the operation is performed so as to condense the water volatilized, it is not found to be impregnated with any essential oil; nor are essential oils usually possessed of such active powers. In some cases, the distilled water, as for example that from the leaves of the cherry laurel, (Prunus lauro-cerasus,) has a narcotic power; in other cases it has none.

These facts are inconclusive. The injury which some of these plants sustain from decoction, while, at the same time, their powers are not communicated to the water distilled from them, is probably to be ascribed not to the dissipation of a subtle volatile principle, but rather to changes which its principles suffer, and probably principally to the oxygenizement of its extractive matter. And where the narcotic power is communicated to water by distillation, some singular facts lately discovered appear to prove, that it depends on the presence of a well-known substance, the Prussic acid. It had always been observed, that this acid has even in a high degree the peculiar fragrant smell of peach blossoms; and it had also been observed, that the same smell, more or less faint, is perceptible in the distilled waters from the leaves of the cherry-laurel, the seeds of the bitter almond, and some similar vegetables, all of which are more or less narcotic. Bohn at length found, that when potassa was added to the water distilled from the bitter almond, it acquired the property of forming a blue precipitate with solutions of iron,—the sure indication of the presence of prussic acid. Schrœder confirmed this, and found farther, that the same acid was contained in the distilled waters of the peach blossom and the cherry-laurel, so that even a prussiate might be obtained from them crystallized, by distilling them from potassa. These singular results were confirmed by Vauquelin and by Bucholz. The latter chemist succeeded in separating prussic acid from the essential oil of the cherry-laurel, by agitation with solution of potassa. And Roloff has since shown, that lime-water, and water of ammonia, with the latter of which Bucholz did not succeed, abstract the prussic acid from the same oil, as well as from the oil of the bitter almond *. It has been found, too, that the prussic acid, in its pure state, is narcotic; and there is therefore every probability in the conclusion, that that quality in the preceding vegetables depends on its presence. But

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* Journal de Physique, tom. lvi. Annales de Chimie, tom. xlv. Philosophical Magazine, vol. xviii.

from this there is no reason farther to infer that it is the narcotic principle; for there is no reason to presume that it exists in other narcotics, and it is itself inferior in narcotic power to some vegetable products.

The existence of a narcotic principle altogether different from this has been inferred from a very different series of facts. Dérosne, in analyzing opium, our principal narcotic, discovered a principle apparently different from any hitherto observed. It was obtained by digesting water on opium: the water dissolves it, along with some other principles, and when the solution is evaporated, a precipitate falls down, which consists of this principle, with resin and extract. By digesting alkohol on the precipitate, the resin and this peculiar principle are dissolved; and as the solution cools, the latter is precipitated in crystalline grains. These may be purified by repeated solution and crystallization: they then assume the prismatic form; are white, free from taste or smell, very sparingly soluble even in hot water, and insoluble in cold water, more soluble in alkokol, and precipitated from this solution by the addition of water *. It proves narcotic, and, according to Dérosne, is more powerfully so than opium. It is also soluble in ether, and in all the acids, as well as in the alkalis; the solutions of it in the acids being precipitated by the alkalis, and those in the alkalis by the acids. It is decomposed by nitric acid, and oxalic acid is formed. Exposed to heat, it melts, and if urged with a strong heat, is decomposed, and affords the usual products of vegetable matter, with ammonia.

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* Annales de Chimie, tom. xlv.

These experiments present results so singular, and according so little with the previous numerous researches on the analysis of opium, that they undoubtedly require to be confirmed by other authorities; and even in their present state, they are far from warranting the conclusion, that it can be regarded as the narcotic principle. There is no proof that it is contained in any other narcotic; and we have even proof, that the narcotic power of some vegetables depends on a very different principle,—the prussic acid. There is even a strong objection to the conclusion, that it is the principle in which the narcotic power of opium resides; for it does not appear to be possessed of that power in the high degree which we should expect were that conclusion just. One grain of opium produces all the effects of a narcotic; yet the great bulk of the opium consists of other principles, particularly of resinous and extractive matter. How small a quantity, therefore, of this principle must be contained in one grain of crude opium; and of course, what high activity must it be possessed of in its insulated state? Yet, from the experiments, it does not appear to have been much more active than opium itself. The whole subject requires farther investigation; and at present there is no proof, and even little probability of the distinct existence of a narcotic principle; the power of acting on the animal system, and producing those effects from which the definition of a narcotic is derived, arising probably, in common with the other powers which the vegetable products have of producing changes in the functions of life, from modifications of composition which may belong to various principles, and which, there is perhaps reason to believe, are too subtle to be ever detected by chemical analysis.

BITTER PRINCIPLE. It has been supposed by some chemists, that a peculiar principle exists in some of the vegetable bitters, in which their bitterness resides. The properties, however, that have been assigned to it, particularly its equal solubility in water and in alkohol, and its precipitation by certain re-agents, appear to prove, that what has been considered as such is a variety of extract, slightly modified, perhaps, by intermixture with other principles. And were even its existence established, the name that has been given to it, implying that it is the principle of bitterness, can with no propriety be assigned to it, since so many substances possess this quality, in which it has not been proved, and can scarcely even be supposed to exist.

A peculiar substance, which is artificially formed from certain vegetable and animal products, and has been named Bitter Principle, has a better claim to be considered as a distinct substance. There is no reason, however, to believe that it is ever naturally formed, or that it exists as a vegetable principle; and as a product of chemical action, particularly of the action of nitric acid on animal matter, it will afterwards fall to be considered.

COLOURING MATTER. It has been supposed, that a peculiar proximate principle exists in vegetables, in which their colour frequently resides, and which has hence received the name of Colouring Matter. In this opinion there is a degree of obscurity and vagueness. Colour being merely a secondary quality, which may reside in any principle, and which often is exhibited by principles of the most opposite kind, there appears no reason to suppose, that there is a distinct principle to which it exclusively belongs. And under this point of view, this conclusion is undoubtedly just. At the same time, we find, that many vegetable products, possessed of deep or of vivid colours, agree in certain chemical relations: the colouring matter can be abstracted from them by the application of certain solvents; can be still farther transferred from these solvents, to other substances exerting affinities towards it; and this, without it being always possible to refer the phenomena to actions exerted to any known proximate principle. In general, this colouring matter appears most nearly allied to the extractive principle; yet it sometimes possesses properties which cannot be referred to this. Farther investigations must determine with more precision its varieties, and their relations to the other vegetable principles. In the obscurity which at present prevails with regard to it, it seems preferable so far to generalize the facts on this subject as to state them in connection, without assuming decidedly, that the principle to which they relate is perfectly uniform and distinct from every other. These facts, too, are of importance from their connection with the arts of dyeing and pigment-making, of which, as being strictly chemical, it is necessary to take notice.

The colouring matter of vegetables is scarcely ever found insulated, but is mixed or combined with other principles. In this state it exists in the leaves, and flowers, in the bark, and in the wood of the stem and roots. It is extracted, and obtained more pure by the action of those agents which are capable of dissolving it.

In many cases, water, cold or warm, is sufficient for this purpose. If logwood, brazil wood, madder, weld, or quercitron bark, for example, be macerated in water, the matter on which the colour depends is dissolved; a transparent solution, more or less deeply coloured, is obtained; and, by repeating the maceration with water sufficiently, nothing at length remains but the mere ligneous fibre.

Sometimes, however, the colouring matter is not soluble in water. It is then frequently soluble in alkohol; and in a few substances, as in the alkanet root, is even best dissolved by oils essential or expressed. Frequently, too, the extraction of the colour is facilitated by the action of other substances, as, for example, the alkalis or acids; and some even can be dissolved only by the acid of these. These differences sufficiently prove, that this matter is not uniform, but that colour is attached to principles of a different nature.

When the colouring matter is in solution, it may be attracted from the solvent by other substances with which it enters into combination: and this in some measure gives it a more appropriate character. There are some substances even which appear in general to exert strong affinities to colouring matter, particularly argil, and some of the metallic oxides. If argil be diffused or boiled in a coloured vegetable infusion, it often happens that the colouring matter combines with it, and leaves the water of the infusion perfectly colourless. Or if alum be dissolved in a coloured infusion, and it be decomposed by the addition of an alkali, the argil in the moment of its precipitation attracts the colouring matter, forms a coloured precipitate, and if the due proportions have been observed, the liquid will remain colourless. In like manner, if a coloured infusion be boiled with a metallic oxide, it often happens that the colouring matter is attracted by the oxide. Thus, Berthollet obtained combinations, by this process, of the colouring matter of logwood, and other dye-stuffs, with oxide of copper, and oxide of tin *. Or if certain metallic salts be dissolved in the infusion, and be then decomposed by an alkali, the oxide in precipitating equally attracts the colouring matter. It is from similar affinities to the colouring matter that it is often attracted by linen, cotton, silk, or wool, from its solutions; and even where the affinities of these are not sufficiently powerful, they may be rendered capable of attracting it, or the combination may be rendered more permanent by their being impregnated with another substance, which has towards it a still stronger attraction.

The shade of colour of any substance, and even frequently the tint of colour, are altered by chemical agents. The alkalis, acids, and various neutral and metallic salts, exert operations of this kind. By some even the colour is much weakened or altogether discharged. Light, it is well known, proves always injurious to the permanence

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* Annales de Chimie, tom. i. p. 239.

and brightness of vegetable colours; so does exposure to the air; and the power of the oxymuriatic acid in destroying them is still more energetic.

ON the principles now stated, rests in a great measure the art of dyeing, the processes of which are in general merely arrangements founded on the affinities of colouring matter, in consequence of which colours are extracted, modified, transferred to the cloth, and rendered more permanent.

This view of the processes of dyeing, which reduces them ultimately to exertions of affinity between the colouring matter and the substance dyed, was only gradually established. The theory that was adopted by the older chemists was rather mechanical. It was imagined, that the colouring matter was merely lodged in the pores of the cloth; and, according as the pores were more or less numerous, of a greater or less fineness, or subject to other modifications, the cloth, or the thread composing it, would be more or less easily dyed; and the action of substances facilitating the dyeing was supposed to depend on the changes they produced on this mechanical structure. This was the theory of Hellot. It was sufficiently obvious, however, that from any operation of this kind, the colouring matter could not be permanently fixed in the cloth, so as to withstand the action of its usual solvents; and the details of the art received only vague explanations from this hypothesis.

Dufay appears to have first formed a proper conception of these operations. He observed, that unless some species of affinity or attraction be supposed between the colouring matter and the substance receiving it, cloth immersed in a dyeing liquor could never receive a deeper colour than that of the liquor itself; whereas the liquor has always the deepness of its colour diminished, and, if certain proportions are observed, it becomes limpid, and the colouring particles are entirely transferred from it to the cloth, "which seems to indicate," says he, as Berthollet has quoted his opinion, "that the ingredients have less attraction for the water, than for the particles of the wool."

Bergman gave this view, however, with much more precision, referred the phenomena of dyeing entirely to chemical principles, and established this on experiment. He had immersed pieces of wool and of silk in a solution of indigo in sulphuric acid largely diluted with water. He observed, that the wool was very speedily dyed, and that if the proper proportions were observed, the solution in which it was immersed was nearly or entirely deprived of colour. The silk was dyed more weakly; it only lessened the colour of the solution, but did not abstract it entirely. These phenomena he ascribed to the different forces of attraction exerted by these substances towards the colouring matter. In consequence of such an attraction, the sulphuric acid had dissolved the indigo; the silk exerted, however, to the particles of the indigo a still stronger attraction than the diluted acid did in which they were dissolved: it therefore abstracted them from the fluid. And the wool did this still more rapidly and completely, as having to these particles a still stronger attraction *.

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* Opuscul. vol. v.

The difference in the forces of affinity of the different materials of clothing for the various kinds of colouring matter employed in dyeing are so considerable, that they vary, not only in the facility with which they are dyed, and the deepness of colour they assume from the same dyeing liquor, but frequently one will receive no colour from a composition which will give another a deep tinge. Cotton, for example, receives scarcely any colour in a bath in which wool is dyed scarlet. Wool is that which appears to have the strongest attraction to colouring matter; next to it is silk, then linen, while cotton has the weakest, and is therefore in almost every case dyed perfectly with most difficulty. Animal matter appears therefore to have a stronger attraction to the colouring particles than vegetable substances have; and this shews some analogy between colouring matter and tannin.

But even when the substance to be dyed has little or no attraction to the matter on which the colour depends, so as either not to be capable of abstracting it from its solvent, or of retaining it with such force as to form a permanent dye, methods have been discovered of compensating for this, and of communicating to it the colour, and rendering it permanent. This is done by impregnating it with some substance which shall serve as a bond of union between them. Such substances are, in the language of the art, denominated Mordants. Their use is essential in almost all the processes of dyeing, and the discovery of them has been altogether empirical, or without any knowledge of the principles on which they operate. Macquer seems first to have given clearly the theory of their actions: where they have been used, he observes, " it is not the stuff immediately which takes the colour, but the earthy or metallic part of the mordants; so that when stuffs are well dyed by these processes, it is owing to those coloured precipitates being capable of adhering to them more or less forcibly." Mordants, therefore, are substances which on the one hand have an attraction to the matter to be dyed, and, on the other, to the colouring matter, and which thus serve to unite them. Without their use, either the colouring matter would not be at all attracted, or attracted so weakly that in washing the cloth it would be again removed.

The mordants are numerous. The principal are alum, acetate of argil, muriate of tin, sulphate of copper, and of zinc, acetate of copper, oxide of arsenic, tannin, and certain animal substances. Of those of the saline kind, it is not so much the entire salt, as its earthy or metallic base that serves to fix the colouring matter; and in the course of the process it is accordingly often, perhaps always, disunited from its acid. Hence the extensive application of alum and of the solutions of tin as mordants, from the powerful affinities of argil and oxide of tin to colouring matter.

Sometimes mordants are employed rather to heighten the colour, or give it more brilliancy, or communicate a particular shade. In this case the operation is obviously altogether different, and these ought to be distinguished by a different appellation. Besides the substances already enumerated, the sulphuric and nitric acids, and even the oxymuriatic acid, in small quantity, are employed with this view.

Mordants are susceptible of a great variety of applications, with regard to the various dyes; and the different cloths, and the proper management of them, constitutes a great part of the art of dyeing. They are used, either by previously impregnating the cloth with them, or by mixing them with the dyeing materials, or sometimes both methods are conjoined. There are also numerous varieties in the composition of the dyeing materials, a number of substances being often mixed, in order to procure a particular colour or shade. This evidently admits of no abridged account; and I must refer, therefore, for any details with regard to it, to the scientific treatise of Berthollet, on the Art of Dyeing.

THE art of cloth-printing or calico-printing, in other words, of dyeing in certain colours particular spots of the cloth, or figures impressed on it, while the ground shall be of a different colour or entirely white, affords perhaps the most direct and obvious illustration of the application of these principles.

The mordant which is principally used in this process, is the acetate of argil. It is prepared by dissolving 3 lbs. of alum and 1 lb. of acetate of lead, in 8 lbs. of warm water. An exchange of the principles of these salts takes place: the sulphuric acid of the alum combines with the oxide of lead, and the compound thus formed being insoluble, is precipitated: the acetic acid remains united with the argil of the alum in solution. There are added at the same time, 2 ounces of the potash of commerce, and 2 ounces of chalk; the principal use of which appears to be, to neutralize the excess of acid that might act on the colouring matter and alter its shade. The superiority of this acetate of argil as a mordant, to the cheaper sulphate of argil or alum, arises principally from two circumstances,—from the affinity between its principles being weaker, in consequence of which the argil more easily separates from the acid, and unites with the cloth and the colouring matter; and, 2dly, from the acetic acid disengaged in the process, not acting with the same force on the colouring matter as the sulphuric acid would do. The acetate being also very soluble, and having little tendency to crystallize, can be more equally mixed and applied. The discovery of this mordant, so essential in the art of calico-printing, was altogether accidental, or rather empirical. The recipes of the calico-printers were at one time very complicated: different articles were from time to time omitted or changed, until at length the simple mixture of alum and acetate of lead was found to answer as a mordant equally with compositions more complicated: and even after its discovery, its operation for a time was far from being understood by the artist.

The mordant thus prepared, is thickened with gum or starch; or in this country, within these few years, with the mucilage prepared from lichens scalded and boiled with a little potash. It is applied by wooden blocks or stamps to the parts of the cloth on which the figures cut in the stamp are designed to be impressed, or by a pencil, if more delicate lines are to be traced. The cloth is afterwards dried thoroughly, is washed in warm water to remove the mucilage and the superfluous mordant, and is then dipt in the dye liquor, suppose it to be an infusion of madder; the whole is dyed, but the parts which have been impregnated with the mordant receive a brighter colour than the part which has not: the colour too of the former is permanent, while that of the latter is fugitive. It is discharged by subsequent boiling with substances having a weak attraction to the colouring matter, principally with bran, and by exposure on the field, repeating these alternately. The ground of the cloth is thus at length rendered white, while the colours of the parts on which the mordant has been impressed, representing of course the design on the stamp, remain with little or no alteration.

With this mordant, madder gives the various shades of red; with weld or quercitron bark, the shades of yellow; and with logwood, a rich but fugitive purple. To diversify the colours, another mordant is likewise employed,—the acetate of iron, applied in precisely the same manner. With madder or logwood it gives black, and by dilution, different shades of purple; with weld, olive, and with quercitron bark, brown. Mixtures of these are also made, which give other colours. Haussman has also recommended as a mordant, acetite of tin.

Sometimes after the whole cloth has been permanently dyed, by having been impregnated with the mordant, the colour is discharged from certain parts, by stamping these with a weak acid liquor: after being washed, these are again stamped, either with the same or with a different mordant, and dyed with different materials; and thus the most difficult kind of cloth printing is effected, where the ground is coloured, and at the same time impressed with a design in different colours. By combining these methods too, and by dextrously applying to different parts of the cloth different mordants, by stamps adapted to each other, so as to form a regular design, different colours are impressed either on a white or coloured ground.

The formation of the vegetable pigments, or what are named Lakes, depends on the same principles, and affords too a very perfect exemplification of the affinities of colouring matter. The colour of any vegetable matter is extracted by its proper solvent, generally by water; and there is added to the solution, some substance capable of attracting and combining with the colouring matter, so as to form an insoluble precipitate. Thus, if alum be dissolved in an infusion of brazil wood, and an alkaline solution be added, the argillaceous earth is precipitated, and carries down with it the colouring matter, forming therefore a lake. Similar lakes are formed from other coloured vegetables, as from quercitron, turmeric, &c. And the most beautiful of them, carmine, is prepared by a similar process from cochineal, a colouring substance of animal origin. It is not always necessary even, that the colouring matter should be in a state of solution. It is sufficient if it be suspended in water. Sir H. Englefield has shewn, that if the colouring matter of madder be in this state of suspension in boiling water in which alum is dissolved, on adding carbonate of potassa the argil is precipitated, and attracts the colouring matter, forming a very rich lake *. Sometimes too metallic oxides are employed as the basis of such pigments, particularly oxide of tin; muriate of tin being added to the coloured infusion, and being decomposed by an alkali: and Guyton has re-

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* Nicholson's Journal, vol. x. p. 215.

commended oxide of tungsten, as affording a basis for lakes superior to any other, both in the brightness and permanence of the colour *.

The vegetable substances used in dyeing are extremely numerous. The colouring matter of the greater number of them, such as all the woods and barks, logwood, brazil wood, weld, quercitron, &c. appears to approach in its characters to extract, and admits therefore of few observations as to their chemical history farther than what have been already stated. Logwood, the wood of the Hæmatoxylum Campechianum is of a bright red colour, and affords to water very easily its colouring matter; its infusion having, with the red, a purple tinge: it is used principally for giving purple dyes, its colour being modified by the different mordants; and it also enters into the composition of the black dyes. Brazil wood, the wood of the Cæsalpina crispa, gives to water a bright red colour, and the colouring matter is easily attracted by argil and the metallic oxides, the latter frequently modifying the colour. The alkalis give to it a violet tint, and the acids precipitate it of a fawn red colour. It is much used both in dyeing and in the formation of lakes. Madder, the root of the Rubia tinctorum, is another red dye, the colouring matter of which is extracted, though rather partially, by water, and of different shades, in repeated macerations, so that at length it gives only a fawn colour; and even after these successive infusions, it still retains much of the colouring matter, which may be extracted by the action of an alka-

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* Annales de Chimie, tom. xxx. p. 185.

li. Alum forms in its infusions a brownish red precipitate; and the remaining liquor, when an alkaline carbonate is added to it, gives a blood-red precipitate, which, by an excess of alkali, is redissolved. It is much used both in dyeing and calico-printing, giving numerous shades of red, according as it is combined with different mordants. Quercitron is the internal bark of the Quercus nigra: it yields its colour, which is yellow, by infusion to water, and by the common mordants, alum and muriate, gives a permanent dye. It is now much used as a substitute for Weld, the stalks of the Reseda luteola, which were formerly used to furnish a yellow dye, being combined with alum and tartar as mordants, and which also was sometimes combined with madder, to obtain orange and other shades. Fustic, the wood of the Morus tinctoria, affords another yellow dye: its decoction in water is of a reddish yellow colour, and it gives a yellow dye to cloth, which, even without the aid of mordants, is permanent; by the use, however, of alum, tartar, and muriate of tin, the colour is rendered brighter. Sumach, the shoots of the Rhus coriaria, is used for giving a fawn colour, which it does alone when merely boiled in water. With acetate of argil, it gives a yellow; and as it contains a portion of tannin, it enters sometimes into the composition of the black dyes, and is likewise used as a mordant, to modify other colours, or render them permanent.

All these substances agree nearly in their chemical qualities; and their colouring matter, which exists in them attached to the ligneous fibre, and more or less mixed with other principles, appears to be very similar in its nature to extract. But besides these, there are some other substances, the colouring matter of which exhibits very different properties, and can scarcely be reduced to any known principle.

The most important and singular of these is Indigo, the produce of different species of the genus Indigofera, which are cultivated for its production in America and the West Indies. It is in some measure an artificial preparation. The plant being cut, when ripe, is put into large troughs or vats, with a quantity of water, and pressed down. It undergoes a species of fermentation, and a quantity of aërial fluid is disengaged, partly inflammable, and said to be a mixture of carburetted hydrogen and carbonic acid. The water becomes turbid, from the formation or extraction of the colouring matter; and when the fermentative process appears to have been sufficiently advanced, it is drawn off into another vat, where it is kept constantly agitated, to promote the separation of the colouring particles, and the disengagement, as is supposed, of a quantity of carbonic acid. Towards the end of this stage of the operation, a portion of lime-water is added, which still farther favours the separation of the colouring matter. It begins, therefore, now to subside. The liquor is withdrawn into another vessel, in which the deposition is allowed to go on: the clear liquor above, which is of a yellow colour, is drawn off: the semi-fluid sediment at the bottom is received into linen bags, through which the remaining fluid strains: the indigo remains in the state of a paste, which is dried by exposure to the air, excluding the solar rays. It differs considerably in its qualities, according to the species of the plant, its state with regard to maturity, and the care and skill with which the operation has been conducted. The rationale of the process by which it is prepared is by no means well understood. The plant, by expression or infusion, affords only a green colouring matter previous to the fermentation; and we have no precise facts from which it can be determined how this fermentation is so easily excited, what are the changes it occasions, and how these are connected with the production of the colouring matter.

Indigo is of a very rich blue colour, varying however in its shade in different specimens. It is light and friable, has a smooth fracture, is tasteless, and has scarcely any perceptible smell.

From Bergman's experiments it would appear to be a heterogeneous substance, since besides its pure colouring matter he found it to contain gum, resin, an earthy matter, and oxide of iron. The proportions in 100 parts were, 12 of gum, 6 of resin, 22 of earthy matter soluble in acetous acid, 13 of oxide of iron soluble in muriatic acid, and 47 of pure colouring matter. It is not easy to determine how far any of these is essential to it, or at least uniformly present, or how far they may be regarded as adventitious. Bergman was disposed to consider the iron as essential to it, and even as contributing to the colour; but, as Berthollet has remarked, the method he used to discover it led him to exaggerate its quantity: and by far the greater part of what he did abstract by the action of muriatic acid was removed without affecting the pure colouring matter.

Indigo yields to water its mucilaginous part: the pure colouring matter is not at all dissolved. By the action of water, the inferior kinds of indigo, according to Quatromore, are improved in their quality, probably by the abstraction of the mucilaginous and extractive matter. The colouring matter of indigo is equally insoluble in alkohol, or in ether, a small portion of resin only being dissolved.

The action of acids on indigo is more energetic and important. Concentrated sulphuric acid dissolves it even in the cold, eight parts of the acid dissolving easily one part of indigo: the solution appears black, from the deepness of its colour, and even when largely diluted with water retains a deep blue colour. It is this solution diluted with about 16 parts of water that is known by the name of Liquid Blue, and that forms also the Saxon blue dye. The colour is changed to a green, as Bergman found, by the action of a number of substances upon it; as by sulphurous acid, vinegar, ammonia, alkaline sulphurets, sulphate of iron; and by some of these the colour was entirely destroyed. As all these might operate by abstracting oxygen, and as some of them are even powerful in de-oxidizing it, it appeared probable that it is to this operation that the change of colour from the blue to the green is owing; yet there are other facts not easily reconciled with this, the blue being changed to a green, or being even entirely destroyed, by other substances which can scarcely be supposed to exert any such agency, as by soda and potassa, and black oxide of manganese.

The alkaline carbonates throw down from the solution of indigo, in sulphuric acid, a blue powder, which Bergman named Precipitated Indigo.

Nitric acid acts on indigo, not merely as a solvent, but decomposes it. The action, when the acid is concentrated, is even so violent as to inflame it; and when diluted, it still acts on it forcibly, and with effervescence; the indigo becomes of a brown colour, and the residuum amounts only to the third part of the original weight. Haussman, in his experiments on indigo and its solvents *, discovered, that by the action of diluted nitric acid on indigo, a substance is formed, which remains in the state of a coagulum, which, freed completely from nitric acid by washing, formed a brown-coloured viscous mass, of a very strong bitter taste, requiring a large quantity of water for its solution, and more soluble in alkohol. This is the substance which has received the name of Bitter Principle, as has been already remarked, and which, as a product likewise of the action of nitric acid on different varieties of animal matter, is afterwards to be noticed. A little oxalic acid is also formed; and from Mr Hatchet's experiments it appears, that one of the varieties of artificial tannin is produced, the solution in water of the residual matter becoming turbid, and depositing a tough elastic film, from the action of gelatin.

Muriatic acid does not act on the colouring matter of indigo, but dissolves merely the oxide of iron, and the earthy matter it contains. It dissolves, however, a portion of what Bergman calls Precipitated Indigo, and acquires a deep blue colour. A number of the other acids, as the phosphoric, acetic, and tartaric, act on it in the same manner as the muriatic. Oxymuriatic acid destroys its blue colour, when the indigo is in a state of solution.

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* Journal de Physique, tom. xxxii. p. 161.

The fixed alkalis, dissolved in water, dissolve only some of the substances contained in indigo, but not its colouring matter. The precipitate from the solution of indigo in sulphuric acid, obtained in the manner already described, is dissolved by them easily even in the cold: the blue colour at the same time gradually changes to a green, and is at length destroyed. With the alkaline carbonates the same solution is effected, but the colour is not altered. The action of ammonia and of lime on indigo, in its different states, is the same with that of the pure fixed alkalis.

Indigo, when exposed to heat, swells, emits vapours, and burns slowly, emitting a white flame. The residuum, which amounts to 33 parts from 100, consists of earthy matter and oxide of iron. From the preceding analysis it appears, that of the 67 parts consumed, 47 have been pure colouring matter. This, subjected to destructive distillation, is decomposed: the products from these 47 parts, were found by Bergman to consist of carbonic acid 2 parts, alkaline liquor (composed of carbonate of ammonia dissolved in water) 8 parts, empyreumatic oil 9 parts, and 23 of charcoal, which, burnt in the open air, left 4 parts, about half of which was oxide of iron, and the other half appeared to be siliceous earth. From this analysis it may be inferred, that the pure colouring matter of indigo consists of hydrogen, oxygen, nitrogen, and carbon, the proportion of carbon being unusually large, and such, indeed, as scarcely appears to be contained in any other vegetable principle. This predominance of carbon in its composition appears, too, from the facility with which it yields artificial tannin, when acted on by nitric acid.

The chemical properties of this substance are peculiar, and are evidently such as prevent it from being considered as a variety of any other known principle.

The application of it to the art of dyeing presents some singular phenomena; for although it is not soluble either in alkaline solutions or in lime, yet, by the intervention of other substances, this solution is effected, so as to form a dye-liquor, and the kind of action of these substances in producing this effect is not very evident.

Bergman examined two of the processes of the dyers, by which indigo is dissolved. One consists in mixing indigo with an equal weight of sulphate of iron, and twice its weight of lime, and boiling them in water: the indigo soon dissolves. In the other, a solution of pure fixed alkali is taken, and to this indigo and orpiment or sulphuret of arsenic are added: the indigo is soon dissolved, and the bath becomes green. Bergman supposed, that the sulphate of iron in the one process, the sulphuret of arsenic in the other, operated by communicating phlogiston to the indigo, or, to adapt the explanation to the change of chemical theory, by abstracting from it oxygen; and this appears to be confirmed by the facts which he ascertained, that if the sulphate of iron has been previously boiled some hours in water, in which case we know it becomes more oxidized, it does not promote the solution of the indigo, and that oxide of arsenic is also equally unfit for this purpose. Haussman has in some measure strengthened this theory, by proving, that a solution of sulphuret of arsenic mixed with indigo absorbs oxygen; and in this case, the indigo is reproduced with its blue colour, and precipitated. This has also been confirmed by Berthollet, who has farther observed, what is strictly conformable to the theory, that when cloth is dyed in the indigo liquors prepared by these processes, it is of a green colour, but becomes blue by exposure to the air; and he found, that a piece of cloth, coming out of the vat of a green colour, became blue by dipping it quickly in oxymuriatic acid. He concludes, from these facts, that indigo, in its natural state, contains oxygen, which may be abstracted from it, when it becomes green; that, in this state, it is soluble in solutions of the alkalis, and of lime; that it is again capable of attracting oxygen, when it acquires the blue colour, and precipitates; and that, on these principles, may be explained the usual processes by which this substance is applied to dyeing. When dissolved by sulphuric acid, it is evidently in a different state, not being deprived of oxygen, but retaining its blue colour, which therefore the cloth at once acquires; yet, even in this solution, the indigo, as Berthollet remarks, appears to have suffered a slight de-oxidizement, and to this he ascribes the solubility in alkalis of the precipitate thrown down from this solution.

WOAD is a substance produced by a process somewhat similar to that followed in extracting indigo, and bears some resemblance to it. It is extracted from the Isatis tinctoria and Isatis Lusitanica. The plant is cut down, washed, and dried in the sun: it is then ground in a mill, and reduced to a paste. Of this heaps are formed, which are covered so as to secure them from rain. This paste, after having remained a fortnight, is turned, and its different parts mixed: it is then made into round balls, which are deprived of their moisture by exposure to the air and sun. These balls, heaped on one another, gradually become hot, exhale an ammoniacal odour; and the heat is increased by watering the heap slightly until the balls are reduced to a coarse powder. In this state woad is used; it gives a blue colour, which is permanent, but has not the beauty of that from indigo. If this plant, however, be subjected to the same process as that followed in preparing indigo, it affords a blue colouring matter precisely the same *; and there can be little doubt, therefore, that the colouring matter of woad is indigo more or less perfectly prepared.

ANNOTA is prepared from the seeds of the Bixa orellana, by bruising them, and keeping them in water until they ferment. A colouring matter is formed, of an orange colour, which is dried, and forms a paste more or less hard. It is not perfectly soluble in water, but forms, by infusion or decoction, a liquor of a yellowish red colour, and turbid: the addition of an alkali renders it more soluble, and gives it a bright orange yellow colour. Acids form with this liquor an orange-coloured precipitate; and a solution of alum forms an orange precipitate still deeper in the colour. Annota is more soluble in alkohol than in water; and hence, besides its use in dyeing, it sometimes enters into the composition of coloured varnishes. In dyeing it is always mixed with an alkali.

From different species of lichen, is prepared the colouring matter known under the names of Archil and Litmus, so useful to chemists, as the most delicate test of acidity. There is some degree of obscurity with regard to these. Archil is said to be obtained from the Lichen rocella, and Lichen parellus; but it appears that other species afford a similar substance. The plant is reduced to powder; a quantity of the potash or soda of commerce is added to it; and it is moistened with urine and kept moist by successive additions, for some time: it ferments, and gradually acquires a blue or violet colour; it is then dried *. Litmus or Turnsole is the same substance, apparently in a more pure state: it has been said to be prepared from the juice of the Heliotropium tricoceum; or the Croton tinctorium, with which linen rags are impregnated, and which are afterwards reduced into a kind of paste, containing, according to Fourcroy, soda, according to Chaptal calcareous earth and potash. The latter chemist has remarked, that its colouring matter is of the same nature as archil. The colouring matter is extracted by water; the infusion is of a crimson colour, inclining to violet; if it be kept secluded completely from the air, the colour entirely disappears; but it is very quickly renewed when the air is admitted. It is also soluble in alkohol, and in this solution exhibits the same phenomenon. It is instantly reddened by the weakest acid liquor; and hence the watery infusion of it, or paper stained with this, affords a very delicate test. Its colour is not much altered by the alkalis. In dyeing it communicates only fugitive colours, and hence is used only in modifying or heightening others that have more permanence.

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* Berthollet on Dyeing, vol. ii. p. 72.

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* Nicholson's Journal, 4to, vol. ii. p. 311.

CHAP. III.

OF THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITION OF VEGETABLE SUBSTANCES.

THE changes of composition to which the vegetable principles are liable from the chemical action of other substances upon them, are in a great measure peculiar with regard to each, as are also the changes they suffer from the application of heat, and have therefore been noticed under their individual history. But, besides these, they are liable to certain spontaneous changes of composition, at natural temperatures, arising chiefly from the re-action of their constituent elements. These, as being more general, are to be the subjects of consideration under the present chapter.

THE term Fermentation has been employed by chemists to denote an extensive series of changes of this kind, in which there is an intestine motion of the parts of the body, and which gives rise to new products; and as this general process varies in its pheriomena and results, according to the circumstances under which it happens, or the nature of the vegetable matter subjected to it, three species of it have been distinguished,—the Vinous, the product of which is vinous spirit; the Acetous, which produces acetous acid or vinegar : and the Putrefactive, in which the elements pass off in new combinations in the aërial form. To these I add that species of slow decomposition which some vegetables in a humid state suffer, leaving a predominance of carbon in their composition. These different species of spontaneous decomposition may be considered under different sections.

SECT. I.

OF THE VINOUS FERMENTATION.

BOERHAAVE appears first to have distinguished fermentation into the three species of vinous, acetous, and putrefactive, each being distinguished by its products as well as by the phenomena it presents. He supposed that these three succeed each other in an invariable order, that the vinous always precedes the acetous, and that this equally precedes the putrefactive.

Some facts are in favour of this hypothesis, or there are substances which undergo these successive changes. Many weak vinous liquors, by a continuance of the fermentative process, become sour, or form vinegar ; and vinegar also undergoes decomposition, forms a mould, or passes into a species of putrefaction. But it is not to be concluded, that these three kinds of fermentation invariably succeed each other : Many vegetable substances become sour, which we do not discover ever to assume any previous vinous state ; and a still greater number undergo that decomposition analogous to putrefaction, without having passed through the two previous stages of fermentation: when they do succeed one another, however, the vinous is that which always precedes the others, and which never succeeds them.

The phenomena which occur during the vinous fermentation, have been examined with sufficient accuracy. The liquor, in passing into it, first becomes turbid; a kind of intestine agitation, in which its parts are moved with regard to each other, takes place; a quantity of aërial fluid begins to be disengaged, which in some measure is entangled by the liquid, and with its impurities forms a scum on its surface; the quantity of this gas disengaged continues to increase; the volume of the liquid is augmented; and the temperature is at the same time raised a number of degrees. The gas thus formed is carbonic acid, and its disengagement continues, until the end of the process, more or less rapidly, according to the nature of the fermenting liquor, and according as it is more or less favoured by circumstances. It appears in its evolution to be impregnated with part of the principles of the fermenting liquor, and to retain a portion of these when it escapes in the aërial form. Chaptal long ago observed, that water which had imbibed it by being placed in a vessel in the atmosphere above a fermenting liquor, on being kept for a month in open vessels, is converred into vinegar, while, at the same time, a flocculent matter is deposited; proving, as he remarked, that the carbonic acid gas had carried with it a little alkohol and extractive matter *.

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* Annales de Chimie, tom. xxxvi. p. 27.

According to the experiments of Fourcroy and Vauquelin, the carbonic acid gas disengaged in fermentation is frequently mixed with hydrogen. They found, that the gas disengaged during the fermentation of barley was of this nature; and this even when the barley had been freed from the bran, which they had at first suspected might have been the source of the hydrogen. The wort of the brewers, in fermenting, afforded, however, only carbonic acid; and the hydrogen, therefore, in the preceding experiments, must have been derived from the fecula of the grain *.

After a certain time, a few days, if the quantity of liquor is considerable, the disengagement of gas and the intestine motion to which this gives rise begin to cease, and the liquor gradually recovers its transparency. If now examined, it is found entirely changed in its qualities; it has lost its bland or sweet taste, has become pungent, and acquired a peculiar odour, and is capable of acting more powerfully on the living system, being exhilarating and intoxicating, more or less according to its strength.

This process is altogether independent of any action of the air. It can be carried on in close vessels, and if materials liable to fermentation be put into a bottle to which a bent tube is adapted which terminates under an inverted jar filled with water, carbonic acid gas soon begins to be disengaged, and may be collected. If they be kept, however, in this situation, the fermentation proceeds, as Chaptal has remarked, more slowly than when the vessels

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* Annales du Museum National, tom. vii. p. 16.

are imperfectly closed, being retarded probably by the pressure of the gas; and hence the necessity, in conducting fermentation on a large scale, of admitting a communication with the atmosphere. Too free an exposure is, on the other hand, prejudicial, or occasions a waste of alkohol and aroma *. If the air be excluded, while the gas formed during the fermentation is allowed to escape, Mr Collier has shewn by experiment, that the liquor fermented under this arrangement is stronger, or contains more alkohol, than when fermented in open vessels †.

Of the vegetable proximate principles, saccharine matter is that which passes with most facility and certainty into the vinous fermentation; and fermented liquors are more or less strong, according as the juices from which they have been formed have contained a greater or less proportion of sugar. Certain circumstances, however, are necessary to enable it to commence and proceed. These are, a due degree of dilution in water, a certain temperature, and the presence of some substances which appear necessary to favour the subversion of the balance of affinities by which the principles of the saccharine matter would otherwise be retained in union, or at least would be prevented from entering into those combinations necessary to form vinous spirit. These substances, from this operation, are denominated Ferments.

1*st*, A certain proportion of water to the matter susceptible of fermentation is requisite. If the latter is in large quantity proportioned to the water, the fermentation does not commence easily, nor proceed so quickly; on the other hand, too large a proportion of water is injurious, as causing the fermented liquor to pass very speedily into the acetous fermentation. The proportion employed by Lavoisier in his experiments on fermentation, were four parts of water to one of saccharine matter.

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* Annales de Chimie, tom. xxxvi., p. 11.

† Manchester Memoirs, vol. v. p. 256.

2d, A certain temperature is not less essential; it requires to be at least 50, or rather 55 of Fahrenheit. At a temperature lower than this, fermentation scarcely commences, or, if it has begun, proceeds slowly; and if the temperature be reduced to 32°, it is entirely checked. It proceeds still more rapidly when the temperature is much above 55°, and requires to be checked to prevent it from passing into the acetous stage.

Lastly, though sugar is the matter which serves as the basis of fermentation, and from which its products are formed, the presence of other substances are requisite to the process. It has been often stated indeed, that sugar alone, dissolved in a certain quantity of water, and placed in a certain temperature, will pass into a state of fermentation. It is doubtful, however, if this happens with a solution of pure sugar; and any change which is observed, is imperfect and irregular: nor does the liquor become vinous, but rather sour.

The substance usually added, where an addition is requisite to excite fermentation, is Yeast,—the scum which is collected on the surface, as well as the sediment formed from liquors already in a state of fermentation. This added to a solution of pure sugar, causes it to ferment, and to pass into a vinous liquor.

What, then, is the nature of the matter contained in yeast, which thus excites fermentation, when it otherwise would not take place? This question has often been the subject of investigation, and it is only lately that some light has been thrown upon it.

Lavoisier, in his experiments on fermentation, remarked, that the matter of yeast is a compound of carbon, hydrogen, oxygen, and nitrogen; and is, therefore, so far of an animal nature. From the more recent researches of Fabroni, Thenard, and Seguin, it is proved, that it is a substance analogous to gluten or albumen which exists in yeast, which is derived from those vegetable juices or infusions that without any addition are capable of fermenting, and which excites the vinous fermentation.

Fabroni, as the result of his researches on fermentation, announced, that though saccharine matter is the principle necessary to the vinous fermentation, it does not ferment alone, but only by the aid of another substance capable of acting upon it: this substance is the glutinous or vegeto-animal matter, which exists in the nutritive grains, and which, as he stated, is also contained in the grape, being deposited from its juice. When the deposition is complete, or rather when the glutinous matter is perfectly separated by repeated filtrations, the juice does not ferment, but the sediment mixed with a substance susceptible of fermentation, causes it to pass into this state. The glutinous part of wheat appears, from some of Fabroni's experiments, to be capable of producing either on the must of the grape deprived of its sediment, or on an artificial mixture, the same effect as the sediment of the must, except that the fermentation is more slowly established, and requires a higher temperature and the concurrence of tartar; the last, as Berthollet has remarked, probably proving useful from the solubility communicated by its acid to the gluten. He accordingly found, that a mixture of sugar and gluten entered into fermentation, by adding a little tartar to it. It is this vegeto-animal matter, according to Fabroni, which principally constitutes the yeast of wine or beer: and Rouelle long ago found, that the sediment deposited from wines in fermentation is of this nature, as it affords much ammonia when decomposed *.

Thenard had likewise undertaken the investigation of this subject. Since the juices of certain fruits ferment very readily without the necessity of any yeast, he directed his attention to these, to discover the principle they contained, and which thus promoted the fermentation of their saccharine matter. He subjected to experiment the juice of the gooseberry, which is very susceptible of fermentation. Having pressed it through a linen cloth, it still remained turbid, and held in suspension a slightly glutinous matter, which was separated by filtration and washed with water. This substance, added to a solution of sugar, caused it to pass into the vinous fermentation. Yet after having produced this effect, it still remained, according to Thenard, insipid, insoluble in water and in alkohol, and no farther altered, except that on being subjected to destructive distillation, it afforded no trace of ammonia. It appears to exist in large quantity in the

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{ Annales de Chimie, tom. xxxi. p. 299.
{ Chemical Statics, vol. ii. p. 410.

juice of the gooseberry, not only suspended, but in a state of solution; for when the juice had been filtered so as to be perfectly clear, on placing it at the proper temperature it fermented, and during the fermentation lost its transparency, and threw down a sediment. This when examined was found to be glutinous and insipid: thrown on red-hot fuel it burnt like animal matter: distilled, it afforded carbonate of ammonia: added to a solution of sugar, it caused it to ferment rapidly. It appeared therefore to be a substance perfectly analogous to the yeast of beer. The same substance was found by this chemist to be deposited from the juice of the grape, the cherry, apple, pear, and other fruits, during their fermentation, and those which afforded the largest quantity of it were those which run most quickly into the vinous fermentation. It is always deposited too, as their fermentation proceeds; and a sediment of yeast always appears, according to Thenard, when alkohol is formed.

To this substance he gave the name of Ferment: it is tasteless, does not change the vegetable colours: by desiccation it loses three-fourths of its weight, from the dissipation of water; thus, dried, it is still capable of exciting fermentation, and may be preserved in this state for an indefinite time. It is so little soluble in water, that the water, after standing over it for several hours, on being filtered and added to sugar exerts no action upon it. It is decomposed by diluted nitric acid, is converted into a fatty matter, nitrogen and carbonic acid gases being evolved. Potassa acts upon it as it does on animal substances, forms a kind of soap, and causes an evolution of ammonia. In its humid state it is liable to putrefaction perfectly similar to that of animal matter, and it affords the same products when decomposed by heat, the proportion of carbon being large. From 8 parts, Thenard obtained, by destructive distillation, 1.61 of water, 1.31 of oil, and 1.46 of muriate of ammonia on adding muriatic acid. The elastic fluid disengaged, amounting to 0.33, consisted of carbonic acid, and carburetted hydrogen or carbonic oxide, and the residuum amounted to 2.83 of charcoal *.

It is evident that these researches still leave a degree of obscurity with regard to this principle, since Thenard has not determined whether it is à peculiar one, or whether it is merely vegetable gluten, as Fabroni had suggested, and as several of its properties appear to indicate. There appears every reason to adopt the latter opinion, more especially as the analysis by Fourcroy and Vauquelin of the nutritive grains † has shown, that gluten is not only contained in wheat, but likewise in barley, a grain which is very susceptible of fermentation.

Seguin has lately affirmed, that albumen, whether vegetable or animal, is the true ferment. As the characters, however, of this principle, and the distinction between it and gluten, have been always somewhat vague, it is not improbable, that Seguin understands merely the latter principle. He had discovered it in large quantity in those vegetable juices which pass into the vinous fermentation without yeast: he affirms, that when they were deprived of it, they became incapable of fermenting, and

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* Nicholson's Journal, vol. vii. p. 33.

† Annales du Museum National, tom. vii. p. 1,

that having added to saccharine matter this principle, it fermented, and yeast was deposited. The respective proportions of albumen and sugar, in the different vegetable juices, determine, according to Seguin, the vinous or acetous nature of the product of fermentation, the product being more spirituous the greater the quantity of sugar. He adds, that animal albumen, as the white of an egg, has the same effect. Boerhaave long ago placed this substance among the ferments, or substances which excite fermentation. According to Fabroni, however, neither the albumen of the egg, the insoluble part of the animal fibre, nor glue, has the property of exciting fermentation.

Whatever, however, be the nature of this principle, it must exist both in the sweet vegetable juices, and in the infusions of the grains that have been subjected to malting, since these are capable of passing into the vinous fermentation without the addition of yeast, and even deposite it as the process proceeds.

It has been supposed, that no substance passes into the vinous fermentation except sugar. The nutritive grains, indeed, as barley and others, can be made to afford fermented liquors; but they are always subjected to the previous operation of malting, in which the fecula of the grain is by the process of germination converted into sugar; and this was held indispensable to render them susceptible of fermentation. The practice, however, of the spirit distillers of this country, proves that this is a mistake. They have been accustomed to add to the malted grain which they ferment with the view of obtaining a spirituous liquor, a certain proportion of grain which has not been malted, but merely *mashed*, or ground to powder and infused in warm water; and the proportion of this has even been gradually so much increased, as to exceed considerably that of the malted grain. The infusion obtained from this mixture of raw and melted grain is, by the addition of yeast, made to ferment easily, and affords a liquor pungent and spirituous.

The practicability of thus fermenting from unmalted grain, and the practice itself, though scarcely taken notice of by chemists, appears to have been known in this country for a considerable time. It is mentioned by Dr Irvine, in an essay on fermentation read before a literary society in Glasgow in 1785. He observes, that not only is saccharine matter susceptible of fermentation, but the farinaceous and mucilaginous parts of vegetables also have a share in producing this effect. In their pure state, they can neither be changed into wine nor vinegar; but, when mixed with a little sweet matter, they all ferment together, and may either change wholly into wine, or wholly into vinegar, according to the proportion of sweet matter mixed with them: if the quantity of sweet matter be very great, the farinaceous parts are entirely changed into the same wine with the sweet part: if the quantity of saccharine matter is very small, the whole becomes vinegar, and has little appearance of ever having been in the vinous state. Thus, a quantity of meal from wheat, barley, or oats, whose greatest part is farinaceous, when mixed with water, becomes by fermentation a little acid, but seems never to acquire any of the properties of wine. If the same meal be mixed with a quantity of sugar, or any other sweet matter, it then falls into the vinous state, and the quantity of spirit produced is much greater than the sweet matter alone would have furnished. He then remarks, that the farinaceous substance of seeds is converted into sweet matter by germination, and that many have supposed, that the powers of vegetation only can produce this change. "Certainly, however," continues he, "the powers of vegetable life are no way concerned, or necessary to it. It is not during the growth only of the seed that this change can be effected; but a quantity of the sweet matter produced by the growth of the seed, mixed with a quantity of the same seed ground into powder, and the whole mixed with a proper quantity of water, will all become sweet, and fall afterwards into the vinous fermentation, and be changed into spirits in the same manner as if the whole had been previously altered by the vegetation of the seed. Were it not for this property of the farina, great loss would frequently be sustained by the farmers in unfavourable seasons; grain that has once begun to grow, and whose vegetation has been stopped, can never be made to grow again. Such grain never can undergo any farther malting: when grain has been made to grow in this improper manner, it can hardly be supposed that the change into saccharine matter is perfect or complete. It therefore would be less proper for the vinous fermentation, and would furnish a smaller quantity of spirit than grain which had been perfectly malted. This grain, however, when mixed with a quantity of perfect malt, and fermented, furnishes as much spirit as if the whole had been in the state of malt. The persons in this trade even prefer it to an equal quantity of malt; for in good seasons, when no such half malted or half spoiled grain can be got, they take good grain, reduce it to meal, and mix it with their malt, and are satisfied that they obtain more spirits in this way than from an equal quantity of good malt *."

That fecula alone, or at least mixed with no more saccharine matter than what is contained in the grain, may be made to ferment, is established by the late experiments of Fourcroy and Vauquelin. Six pounds of unmalted bruised barley being treated with alkohol, furnished one ounce two drachms of pure sugar; the same quantity of malted barley, treated in the same manner, having afforded four ounces five drachms. Twenty-four pounds of the flour of the unmalted barley, having been put into a vat with seven times its weight of warm water, and four pounds of yeast, entered into strong fermentation immediately, which continued seven days. The liquor at the end of that time submitted to distillation gave a weak spirituous liquor, which by rectification afforded alkohol. The quantity amounted to twenty-three ounces. Now Lavoisier had established, that 100 parts of sugar give 58 of alkohol; and as the 24 lbs. of unmalted barley contained only 5 ounces of sugar, it follows, that four times more alkohol had been formed than that sugar could have furnished; that of course a large quantity of it had been formed from the fecula in the grain.

Twenty-four pounds of malted barley bruised having been fermented, under the same circumstances as in the preceding experiment, presented the same phenomena, the proportion of alkohol being three times greater than could have been formed from the sugar in this barley †.

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* Irvine's Chemical Essays, p. 318.

† Annales du Museum National, tom. vii.

As fecula consists of the same principles as sugar, differing only in the proportions, it is not difficult to admit, that it may be brought into fermentation, and may afford ultimately the same products as saccharine matter, though it is also possible, perhaps, that even in the process now described, the fecula may proceed rapidly through the intermediate state of sugar, in passing into the vinous fermentation; and it would appear actually to do so, if the observation of Dr Irvine be correct, that when the flour of unmalted grain is mixed with a quantity that has been malted, the whole, mixed with water, becomes sweet.

Our knowledge of the series of chemical changes which constitute vinous fermentation, is still imperfect. Some essential facts connected with it were established by Lavoisier, and a theory given, which, however, more recent investigations have proved cannot be admitted as altogether just.

The properties of the fermented liquor, its odour, pungency, and intoxicating quality, are owing to the presence of a peculiar substance, which can be separated from it by distillation, and which, in a pure state, possesses these qualities in a much higher degree. It constitutes, in the state of dilution in which it is obtained by distillation, vinous spirit, or, as obtained from different fermented liquors, from which it derives some peculiarities of taste and flavour, the spirituous liquors of commerce. These, by certain processes, afford this principle perfectly pure, and the same from all of them: in this pure state, it is the spirit of wine of the older chemists, the alkohol of the modern nomenclature.

To ascertain with more accuracy the changes which happen during fermentation, Lavoisier, instead of operating on any of the sweet vegetable juices, the exact analysis of which is difficult, dissolved a certain quantity of pure sugar in water, and made the solution to ferment, by the addition of a quantity of yeast. He had previously sought to determine the composition of sugar, and found it to be a compound of carbon, hydrogen, and oxygen; he found, that during fermentation, no portion of the water of the fermenting liquid undergoes decomposition; nor is the presence of the air necessary to the process. Since the products are the carbonic acid gas which is disengaged, and the alkohol which is contained in the fermented liquor, it follows from these deductions, that these must be entirely derived from the decomposition of the saccharine matter; that in fermentation, therefore, part of the oxygen and carbon of the sugar combine and form carbonic acid; and that its remaining elements, its hydrogen, with the remaining oxygen and carbon, form the alkohol. This is accordingly the view he gives of the vinous fermentation. "Its effects on sugar are reduced to the mere separation of its elements into two portions; one part is oxygenated at the expence of the other, so as to form carbonic acid, while the other part being disoxygenated in favour of the former, is converted into the combustible substance called Alkohol *."

It follows from Lavoisier's experiments, that 100 parts of sugar require about $\frac{1}{71}$ of yeast, deducting the water which is foreign to it; that it produces a little more than

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* Elements of Chemistry, p. 196.

35 parts of carbonic acid, and that nearly 58 parts of alkohol are obtained by distillation, about 2 parts of acetic acid and 4 of extract remaining.

Independent of objections which may be made to the details of this theory, from the uncertainty of the composition of the substances concerned, so far at least as relates to the proportions of their elements; and independent likewise of the slight correction that must be made, from the fact now established, that fecula, as well as sugar, is capable of fermentation,—an error was committed by Lavoisier, which affects the general theory, from not attending sufficiently to the operation of the ferment or yeast. This he regarded as serving merely to excite the fermentation, and as remaining the same at its termination as at its commencement; but he did not explain in what manner it produced this effect, and it is possible, that its operation may depend on some of its principles entering into combination with those of the fermenting substance.

Fabroni has supposed that the ferment operates in exciting fermentation, by its carbon attracting part of the oxygen of the sugar, forming the carbonic acid, which is disengaged; while the remaining sugar thus partially de-oxidized, enters into combination with its hydrogen and nitrogen, and forms what properly constitutes the vinous or fermented liquor, or gives to it at least its pungency and intoxicating quality. Neither of them, therefore, he alleges, is to be found in the liquor after fermentation, if this has been complete. Of this theory, however, of the mode of action of the ferment, no proofs are advanced, at least none are stated in the abstract of Fabroni's opinion given by Fourcroy *.

Thenard has given a view somewhat similar, though not, perhaps, precisely so, and has endeavoured to support it by experiment. He mixed together a quantity of ferment with five times its weight of sugar, and added water: fermentation commenced, and, in four or five days, all the saccharine matter had disappeared: a quantity of carbonic acid gas was, as usual, disengaged in the progress of the fermentation, and the liquor, on distillation, afforded diluted alkohol. The residue of the liquor, after the distillation, was evaporated to dryness, and a substance obtained, nauseous, slightly acid, and feebly attracting the moisture of the air. The nature of the acid could not be determined, but, according to Lavoisier, it is the acetous which is obtained in such an experiment. Lastly, of the ferment there still remained two-thirds of a substance, which, as Thenard states, he was surprised to find afforded much less ammonia by distillation than the original ferment. From this fact, which appeared to indicate that part of its nitrogen had been abstracted, he concluded, that by mixing it anew with sugar, fermentation would take place, and all the nitrogen would disappear. This accordingly happened: at the end of seven days, the liquor being filtered, a residuum was obtained, which gave no trace of ammonia.

It appearing from these experiments, that the nitrogen of the ferment disappears during fermentation, Thenard supposed, that it might be carried off by the carbonic acid

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* Annales de Chimie, tom. xxxi. p. 299.

gas; but, on collecting this, no nitrogen gas was found to be mixed with it. Since it is not contained, therefore, either in the gas which escapes, or in the residuum, it must have entered into the composition of the fermented liquor. Yet Thenard could not discover it in the alkohol, the essential product of the fermentation, when he subjected it to various modes of analysis with this view. He concludes, however, that it must exist in it; and these experiments lead to the view he has given of the action of the ferment in exciting fermentation. He supposes, that all the carbonic acid disengaged does not, as Lavoisier had concluded, proceed from the decomposition of the sugar: the first portions of it he supposes to be formed from a combination of the carbon of the ferment with the oxygen of the sugar; and the ferment excites fermentation, by abstracting from the sugar a portion of this principle; the equilibrium of its principles being broken, gives rise to their combination in a different manner, so as to form carbonic acid and alkohol: even a part of the hydrogen of the ferment, he supposes, attracts a portion of the oxygen of the sugar; and its nitrogen probably enters, with the remaining elements of the sugar, into the composition of the alkohol. The other principles of the ferment not expended in these combinations, form, he supposes, the small quantity of acetous acid, and the insoluble matter which is precipitated. In confirmation of these views, he farther states, that ferment has a strong attraction to oxygen; that it absorbs it from the atmosphere, or in its pure elastic state, and forms carbonic and acetic acids, the nitrogen being disengaged *.

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* Nicholson's Journal, vol. vii. p. 40.

Seguin has given a very different view of the theory of fermentation. He supposes, that in this process water is decomposed; that its oxygen unites with the carbon of the ferment, and produces carbonic acid; while its hydrogen combines with the sugar, and converts it into alkohol *. The objection to this theory, as Thenard has remarked, is, that by fermentation more alkohol ought to be obtained than there was sugar; whereas little more than half its weight is produced. And besides, the carbon of the ferment cannot be supposed to furnish all the carbonic acid that is disengaged; nor does alkohol contain so large a proportion of oxygen as sugar.

It is obvious, that the facts are not yet sufficiently ascertained to admit of any certain conclusions being drawn, much less of a perfect theory being delivered, since, amid the obscurity which still prevails, various suppositions, *à priori*, perhaps equally probable, might be formed as to the reciprocal actions of substances, the elements of which are so much disposed to mutual combinations, as those concerned in fermentation; and the subject must still remain to be elucidated by farther research.

By the process of fermentation, a number of liquors are formed, all possessed of certain powers, particularly of an intoxicating quality, but differing very considerably from each other in their strength as vinous liquors, their taste, flavour, and other qualities,—differences owing partly to the circumstances under which the fermentation has been conducted, but more to the original substances from which they have been formed. They may be arranged under two divisions, considerably different from each other,—into what are strictly named Wines, formed by fermentation from the sweet juices of fruits, and into the various kinds of Ale or Beer, formed by the same process from the nutritive grains, subjected more or less to the previous process of germination or malting.

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* Nicholson's Journal, vol. vii. p. 43.

Of the Wines, those afforded by the juice of the grape claim pre-eminence. It is highly saccharine, without much acid, or matter liable to afford acid; its flavour is agreeable, and it contains, at the same time, the principle necessary to excite fermentation. Hence it passes readily into that state, and affords a rich vinous liquor. Numerous varieties of these wines are formed from the grape modified by climate, soil, and culture, in consequence of which it is more or less saccharine, and intermixed with other principles from which it derives flavour and other qualities. The product is scarcely less influenced by the manner in which the fermentation is conducted; whether it has been rapid or slow, whether the air has been freely admitted, and the gas allowed as freely to escape, or the reverse; or whether it has been checked before it has been completed. Hence the distinction of sweet wines, or those still containing a portion of saccharine matter; of strong and spirituous wines, in which a rich juice has been completely fermented, so as to furnish a large proportion of alkohol; of sparkling wines, in which a quantity of carbonic acid is retained by the manner in which the fermentation has been conducted, or by its having been put into bottles before this has been complete; and rough or astringent wines, in which some astringent matter originally contained in the fruit is retained. Wines too differ greatly in their flavour, which is derived from the grape, and is much liable to be modified by soil and climate, and which in the different wines is still more varied by the mixture of different varieties of grapes. The colour of wines is derived, not from the juice of the grape, but from the external pellicle: hence colourless wines are prepared from the red grape, by expressing the juice carefully, and allowing none of the husks to remain mixed with it; while, by an opposite practice, or by even macerating the juice, while fermenting, on the husks, colour will be communicated. All wines contain too a portion of super-tartrate of potassa derived from the juice; this they deposite slowly, in the gradual fermentation they suffer in the cask; and to this, as well as to the other changes produced by this slow fermentation, is owing the improvement of wine from age.

Wines are also formed from other fruits, as from the currant, apple, pear, &c. The juices of the currant, gooseberry, &c. contain too large a proportion of acid, and too little saccharine matter, to furnish wine equal to that from the grape, but are improved by adding to the juice, before fermentation, a portion of sugar. Cyder, from the juice of the apple, and perry from that of the pear, retain a considerable quantity of the acid of the fruit, and when well prepared, a large quantity of carbonic acid, which communicates to them pungency and a sparkling quality. There also remains in these liquors a portion of extractive matter or mucilage, which renders them more liable to pass into the acetous fermentation.

The other kinds of fermented liquors, are those formed f[illegible]arley and other grains, forming the different varieties of ale and beer. In the preparation of these, the fecula and mucilage of the grain requires to be altered by the process of malting; both to afford, by the production of saccharine matter, a liquor more easily fermented and stronger, and to render them less liable to pass into the acetous fermentation. The grain is steeped in water for 50 or 60 hours, by which the husk is softened, and a portion is imbibed by its substance. The water is run off, and the moistened grain is spread out on the floor of a chamber, being collected to the depth of 10 or 12 inches, to prevent it from becoming dry: the light too is in a great measure excluded. It begins to germinate, absorbs oxygen, and gives out carbonic acid: in consequence of this chemical action the temperature rises; and to prevent it from rising too high, as well as to render the process as uniform as possible through the whole grain, it is turned up, and is gradually spread into a thinner heap. The germ, in the course of this operation, unfolds, and the plumula gradually elongates, forming what the brewers call the Acrospire. The progress of the process is known by the extent of this elongation, which is permitted to go on for a longer or shorter time according to the quality of the grain, and the kind of fermented liquor that is to be formed. When the plumula is about equal to the length of the seed, the fecula is supposed to be most completely converted into saccharine matter. When it is to be checked, the grain is dried gradually by the heat of a kiln, which is raised gradually, and which for different purposes is raised to different degrees. The whole of these operations constitutes the process of malting; which is obviously nothing more than germination artificially excited, with the view of converting the fecula into saccharine matter, and the theory of which has already been fully considered (page 61, &c.).

The grain, after having been malted, is freed from the small projecting shoots, and is ground to coarse powder in a mill, or crushed between rollers. This is infused in warm water in the mashing tun: the temperature at which this is to be used is considered as of importance, since, if not sufficiently high, the saccharine matter is not properly extracted, while if it be too high, the farina becomes pulpy; the temperature at which the water is generally used is between 160° and 170°. The first portion of water, after a few hours maceration, is drawn off, and a fresh quantity added. These liquors form the wort: this, previous to its fermentation, is boiled with a quantity of some bitter vegetable, generally hops, but frequently also other bitter herbs; the advantage of which, besides the flavour and taste which it communicates, is supposed to be to check the tendency of the liquor to acescency. When the temperature has subsided, a portion of yeast is added, by which fermentation is sooner excited; this, after it has continued a certain time, is checked before it is perfectly complete, at least when the object is to prepare a fermented liquor for drink, and the liquor is drawn off. In this manner are formed the different kinds of beer, ale, and porter; the process being varied with regard to each of these, and different additions being made besides the malted grain. They are of course weaker than wines, and are in general more liable to become flat and acescent, from this circumstance, as well as from the portion of mucilaginous and extractive matter which they contain;

but they are still possessed of the same general qualities, agree in the effects, they produce on the animal system, and afford a portion of alkohol by distillation. Their narcotic power is often, perhaps generally, increased by the addition of certain substances, and is greater, therefore, than is proportioned to their strength as vinous liquors; and it is somewhat modified perhaps, by the bitter matter which the stronger kinds of them contain.

When grain is fermented to afford a wort which is to be subjected to distillation with the view of affording a spirituous liquor, part of it, it has already been remarked, is always used raw or unmalted. The fermentation too is conducted rapidly, and is carried at once to the full extent, so as to obtain the largest produce of alkohol from the matter convertible into it.

From fermented liquors, spirituous liquors are obtained by distillation; all consisting principally of alkohol in a diluted state, but varying in their strength and flavour, as obtained from different substances. Brandy, the purest perhaps of these spirituous liquors, is obtained by distillation from wine: Rum, from the fermented juice of the sugar cane; and from the different grains, what is named Malt Spirit is formed. In this country, to prepare the last of these, the liquor fermented from the mixture of malted and unmalted grain is subjected to distillation, and the weak liquor which is obtained, is rendered stronger and purer by distilling it a second time. The peculiar flavour of these different spirituous liquors, depends probably on a small portion of essential oil, derived from the vegetable matter from which they have been originally prepared, and not altogether changed by the fermentation, or perhaps from combinations established in the course of the processes from which they have originated.

The art of obtaining, by distillation, spirituous from fermented liquors, was unknown to the ancients. It is said to have been discovered by the Arabians, and was practised during the dark ages. The method even of rectifying these, so as to obtain alkohol, was known to some of the earlier alchemists.

It was generally supposed, that the alkohol produced by distillation from fermented liquors pre-existed in them, and being very volatile was merely separated by the heat. Fabroni, however, advanced the opinion, which indeed had been before suggested, that it is formed from the principles of the fermented liquor during the distillation; and supported this by the result of experiments, in which, if alkohol be added to wine, it can be discovered, while by the same method alkohol cannot be detected in unmixed wine. The manner of making the experiment by which this is established, is to take fresh wine with which one hundredth part of alkohol has been mixed, and to add to this as much potash as is found by a previous experiment to be necessary to precipitate the resinous colouring residue. It is then strained and put into a glass tube graduated into 100 equal parts, and as much potash is added as it can dissolve. The hundredth of alkohol which had been added, will then be seen to rise, and swim distinctly on the surface of the alkaline solution, and will be of the same degree of strength, and in the same proportion that had been added, if the experiment is performed sufficiently quickly to lose nothing by evaporation. "Now if by this means," says Fabroni, "I procure only the same quantity of alkohol from the wine that I knew it contained before, and no more, it appears to me, that I have a right to conclude that that which I obtain from the same wine by distillation, did not exist in it before, but that it is the operation of distillation which forms it." He adds, that by the same method he could not discover in new wine any alkohol, though he could obtain from it 20 or 25 parts of brandy in 100, by distillation *.

This experiment, however, is not perhaps perfectly conclusive; for admitting the accuracy of the result, (though it must be considered as rather singular, that one hundredth of alkohol should be capable of being separated again from a liquor in which it is dissolved, and that without any loss), it is perhaps possible that the alkohol formed during the fermentation may be in more intimate combination with the principles of the wine, which will impede its separation, than a portion of alkohol newly added and immediately operated on will be. Chaptal has well remarked, in reference to this question, that a similar phenomenon is to be observed when alkohol is mixed with water: this diluted alkohol has not the same taste with distilled spirit of the same strength, in which probably the combination is more intimate; and we know, indeed, that the increase of density from such a mixture, does not at once attain its maximum; proving, therefore, that the combination is not at once complete. It may be added, that it is not very probable that at a temperature so moderate as that at which the spirit distils off, new combinations

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* Annales de Chimie, tom. xxxi. p. 303.
Nicholson's Journal, 4to, vol. iv. p. 46.

should be established from which it would be formed: nor is this heat greater perhaps, than that which a mixture of alkohol with water, of the same strength, would require to cause it to boil. And the fact, that the alkohol has the powers of the fermented liquor, and has them in a much higher degree than that liquor has, favours the conclusion, that it exists in it, and communicates to it these qualities. Nor is there any force in the argument which has been advanced against this opinion, that by mixing the product of the distillation of a fermented liquor with the residuum, we do not re-produce it; since it is obvious, that the high temperature which prevails, especially towards the end of the distillation, might have so altered the combinations as to render this impracticable. It appears, on the whole, most probable, that alkohol pre-exists in wine and other fermented liquors, but probably not insulated, but combined, as Chaptal has observed *, with the colouring and extractive matter, and all the other constituent principles of the wine; so that when, by the application of heat, the combination is weakened, these principles are separated, and the most volatile rises first, forming alkohol, which, as the distillation proceeds, becomes more and more diluted with water.

Yet so nearly do these opinions approximate, that even this, it appears, may be understood as implying that the alkohol is actually formed; at least it is in this sense that the opinion of Chaptal has been considered by Berthollet, and adopted by him. "It appears to me," says he, "that alkohol has not at first an insulated existence

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* Philosophical Magazine, vol. xi. p. 131.

in wine, although a little may be found in generous old wines, but that, laying aside the tartar and the other acids, this liquor must be considered as an uniform compound, in which, according to the opinion of Chaptal, the properties of hydrogen are predominant: heat disposes this elastic principle to separate, but its elasticity being balanced by the affinity which retains it in combination, a division of the elements takes place in the ratio of these two forces, and a liquid passes in distillation, in which the properties of the hydrogen have become much more predominant, while the other principles of greater fixity remain and form the extract: a second distillation of the spirituous liquor separates the water, which was only retained with the alkohol by a weak affinity *." The arguments, however, which I have already stated, and particularly the observation, that wine possesses the same power as alkohol in acting on the living system, appears to me to render more probable the conclusion, that the alkohol exists fully formed in the wine; for this similarity of power could scarcely be expected, were its elements only contained in the wine in other combinations.

Chaptal, in his analysis of wines, found †, that the alkohol they afforded varied much in quantity: some rich wines furnished a third of spirit, while some weak wines did not give more than a fifteenth. He found, besides the alkohol, a portion of acid always present,—all wines reddening test paper: it appeared from his experiments, to be the malic acid, with a small portion of the citric: it is

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* Chemical Statics, vol. ii. p. 426.

† Philosophical Magazine, vol. xi. p. 128. 368.

contained in larger quantity in the wines from other fruits, as cyder; and predominates in the fermented liquors from grain. He supposes, with some probability, that it is in a great measure the cause of the disagreeable flavour the spirit distilled from them has, compared with that distilled from wine: this spirit, at its first distillation, he found always acidulous. The richer wine is in spirit, the less malic acid does it contain; and hence the richest wines furnish the most agreeable and purest spirit. Wines also always contain a portion of tartar, derived from the grape, and which they slowly deposite. They hold dissolved too, a quantity of extractive matter, derived from the same source, and which is more abundant in new than in old wines. To these principles is to be added, the colouring matter derived from the pellicle of the grape, and dissolved by the alkohol, as the fermentation proceeds. This is often slowly deposited, and may at once be precipitated by adding lime, which combines with the malic acid, and at the same time attracts the colouring matter. This precipitate is insoluble in water, either cold or warm, and alkohol likewise has scarcely any effect on it. Lastly, there is the aroma of wine, or principle which gives it its peculiar flavour, and which is so delicate as to be destroyed instead of being separated by heat.

FROM the spirituous liquors of commerce, ALKOHOL may be obtained; and having considered the production of this principle, it is now necessary to attend to the properties it exhibits in its pure and insulated state.

The process for obtaining it in this state, varies somewhat according to the kind of spirituous liquor from which it is extracted. The purer kinds, as brandy, may afford it merely by repeated distillations, a portion of the water remaining at each distillation in the retort, with any small quantity of other matter contained in the spirit; the alkohol passes over less and less diluted, and may thus at length be obtained pure, or at least can be obtained in such a state by adding, in the latter distillations, a little potash to abstract the water more completely. When it is to be obtained, however, from malt spirit, which it always is in this country, the process is rather more complicated.

The spirit is first distilled, to free it from the greater part of the water mixed with it, and the nauseous oily, or extractive matter derived from the grain. The alkohol passes over, still however containing a little of this, and also a portion of water. There is now added to it sub-carbonate of potassa, in the proportion of an ounce to 1 lb. of spirit; the sub-carbonate having been dried perfectly, and indeed raised nearly to a red heat, and added before it is quite cold. It attracts much of the water, and forms a solution of greater specific gravity than the purer spirit, which, therefore, subsides to the bottom. The spirit is poured of, and is distilled from a little of the same alkaline carbonate, (about half the quantity before employed,) with a gentle heat, stopping the distillation before it come to dryness.

The spirit thus obtained, though very strong, has a disagreeable flavour, derived from the alkali. To free it from this, and to obtain it still more pure, it is subjected to another distillation, with the addition of a small quantity of common alum, about one drachm to the pound;

the acid of which attracts the small quantity of alkali it had held in solution: and in this distillation a little recently prepared charcoal powder is frequently added, to remove more completely any unpleasant flavour.

Alkohol obtained by such a process, is of a specific gravity of about 0.835, and is sufficiently well adapted for the uses to which it is applied in pharmacy, as well as for many chemical purposes. It still has a portion of water, however, combined with it, which may be abstracted by repeated distillations from substances having a strong affinity to water. Potassa, either pure or in the state of sub-carbonate, and muriate of lime, are those generally employed. With pure potassa the alkohol may be so far concentrated, as to be of the specific gravity of 0.815; and Dr Fordyce furnished a quantity used in the first experiments of Gilpin, at .813. By using muriate of lime, it may be obtained still lighter. Dr Black brought it to 800: in the tables of Chaussier, it is stated at the temperature of 60° at .798; and Lowitz succeeded in obtaining it at the temperature of 68° at .791. This is the lowest specific gravity at which it has been procured, and therefore the purest alkohol, though it is still uncertain if even at this strength it is perfectly free from water; nor indeed have we any method of determining when it would be so.

The strength of alkohol is best judged of from its specific gravity. It combines with water in every proportion, and undergoes no change in its properties, farther than a change in its density. The specific gravity of the alkohol is always increased by the addition of the water, not only from the greater specific gravity of the latter fluid, but likewise from the accrued density in consequence of the chemical combination. From this last circumstance, the specific gravities of such mixtures cannot be determined *à priori* from knowing what portions of alkohol and of water are mixed together, but must be determined by actual experiment. This is a subject of much importance, from its relation to the strength of the spirituous liquors of commerce; and it has, accordingly, from time to time engaged the attention of many chemists. The labours of Blagden and Gilpin have been most extensive, and the results they have established perhaps the most accurate. Their first report on the best method of proportioning the excise on spirituous liquors was published in the Philosophical Transactions for 1790, in which the specific gravities, from standard alkohol, through the several mixtures of it with water in different proportions, down to equal parts, were given; the experiments having been executed by Mr Gilpin, and the report drawn up by Dr Blagden. In a supplementary report in the Transactions for 1792, the specific gravities of the mixtures in which the proportions of water are larger were given, together with those formerly given and again repeated. And in the volume for 1794, a set of tables were published, showing the specific gravity of every mixture of alkohol and water, from 100 of alkohol to 1 of water, and 100 of water to 1 of alkohol, at the various temperatures from 30° to 80°, with additional columns, expressing their volumes, the diminution they suffer from the combination, the quantity of spirit *per cent.* and the decimal multiplier by which the quantity by measure of standard spirit in the corresponding mixture may be ascertained. It was difficult to determine what constituted pure alkohol, as, although it had been taken at the least specific gravity at which it could be procured, it was possible, that methods might afterwards be discovered of obtaining it at a specific gravity still lower, as has indeed actually happened. It was therefore as well to fix on it of a certain strength as a standard; and as it can always be obtained without difficulty of the specific gravity of .825, this was taken as the standard, the temperature being 60° of Fahrenheit. This standard alkohol consists, according to Mr Gilpin's experiments, of 4.5 of water, and 100 of alkohol of the specific gravity of .814. The following abridged table, formed by Mr Nicholson * from the more extensive tables, shows the specific gravities of the different mixtures of standard alkohol of the specific gravity of .825 at 60°, with the different proportions of water, for every five degrees of temperature between 30 and 80. In the supplementary report, the temperatures were carried even to 100, but those above 80 were omitted in the last tables, probably as being of little utility, and as being unavoidably liable to inaccuracy, from the volatility of the spirit. I have therefore likewise omitted them.

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* Chemical Dictionary.

Heat.	The pure spirit.	100 spirit to 5 water.	100 spirit to 10 water.	100 spirit to 15 water.	100 spirit to 20 water.	100 spirit to 25 water.	100 spirit to 30 water.	100 spirit to 35 water.	100 spirit to 40 water.	100 spirit to 45 water.	100 spirit to 50 water.
30°	.83896	.84995	.85957	.86825	.87585	.88282	.88921	.89511	.90054	.90558	.91023
35	83672	84769	85729	86587	87357	88059	88701	89294	89839	90315	90811
40	83445	84539	85507	86361	87134	87838	88181	89073	89617	90127	90596
45	83214	84310	85277	86131	86905	87613	88255	88849	89396	89909	90380
50	82977	84076	85042	85902	86676	87384	88030	88626	89174	89684	90160
55	82736	83834	84802	85664	86441	87150	87796	88393	88945	89458	89933
60	82500	83599	84568	85430	86208	86918	87569	88169	88720	89232	89707
65	82262	83362	84334	85193	85976	86686	87337	87938	88490	89006	89479
70	82023	83124	84092	84951	85736	86451	87105	87705	88254	88773	89252
75	81780	82878	83851	84710	85496	86212	86864	87466	88018	88538	89018
80	81530	82631	83603	84167	85248	85966	86622	87228	87776	88501	88781

Heat.	100 spirit to 55 water.	100 spirit to 60 water.	100 spirit to 65 water	100 spirit to 70 water.	100 spirit to 75 water.	100 spirit to 80 water.	100 spirit to 85 water.	100 spirit to 90 water.	100 spirit to 95 water.	100 spirit to 100 water.
30°	.91449	.91847	.92217	.92563	.92889	.93191	.93474	.93741	.93991	.94222
35	91241	91640	92009	92355	92680	92986	93274	93541	93790	94025
40	91026	91428	91799	92151	92476	92783	93072	93341	93592	93827
45	90812	91211	91584	91937	92264	92570	92859	93131	93382	93621
50	90506	90997	91370	91723	92051	92358	92647	92919	93177	93419
55	90367	90768	91144	91502	91837	92145	92436	92707	92963	93208
60	90144	90549	90927	91287	91622	91933	92225	92499	92758	93002
65	89920	90328	90707	91066	91400	91715	92010	92283	92546	92794
70	89695	90104	90484	90847	91181	91493	91793	92069	92333	92580
75	89464	89872	90252	90617	90952	91270	91569	91849	92111	92364
80	89225	89639	90021	90385	90723	91046	91340	91622	91891	92142

Heat.	95 spirit to 100 water.	90 spirit to 100 water	85 spirit to 100 water.	80 spirit to 100 water.	75 spirit to 100 water	70 spirit to 100 water	65 spirit to 100 water.	60 spirit to 100 water.	55 spirit to 100 water.	50 spirit to 100 water.
30°	94447	.94675	.94920	95173	.95429	.95681	.95914	.96209	.96470	.96719
35	94249	94484	94734	94988	95246	95502	95772	96018	96315	96579
40	94058	94295	94547	94802	95060	95328	95602	95879	96159	96434
45	93860	94096	94348	94605	91871	95143	95423	95705	95993	96280
50	93658	93897	94149	94414	94683	94958	95243	95534	95831	96126
55	93452	93696	93948	94213	94486	94767	95057	95357	95662	95966
60	93247	93493	93749	94018	94296	94579	94876	95181	95493	95804
65	93040	93285	93546	93822	94099	94388	94689	95000	95318	95635
70	92828	93076	93337	93616	93898	94193	94500	94813	95139	95469
75	92613	92865	93132	93413	93695	93989	94301	94623	94957	95292
80	92393	92646	92917	93201	93488	93785	94102	94431	94768	95111

Heat.	45 spirit to 100 water.	40 spirit to 100 water.	35 spirit to 100 water.	30 spirit to 100 water	25 spirit to 100 water.	20 spirit to 100 water.	15 spirit to 100 water.	10 spirit to 100 water.	5 spirit to 100 water.
30°	.96967	.97200	.97418	.97635	.97860	.98108	.98412	.98804	.99334
35	96840	97086	97319	97556	97801	98076	98397	98804	99314
40	96706	96967	97220	97472	97737	98033	98373	98795	99345
45	96563	96840	97110	97384	97666	97980	98338	98774	99338
50	96420	96708	96995	97284	97589	97920	98293	98745	99316
55	96272	96575	96877	97181	97500	97847	98239	98702	99284
60	96122	96437	96752	97074	97410	97771	98176	98654	99244
65	95962	96288	96620	96959	97309	97688	98106	98594	99194
70	95802	96143	96484	96836	97203	97596	98028	98527	99134
75	95638	95987	96344	96708	97086	97495	97943	98454	99066
80	95467	95826	96192	96568	96963	97385	97845	98367	98991

The specific gravity of the mixtures of alkohol and water is best determined by the hydrometer or gravimeter, of which there are different kinds in use. That of Fahrenheit, improved by Nicholson and Guyton, is probably to be preferred, as the most accurate and delicate *. The other methods that have been employed to judge of the strength of spirituous liquors, as well as of pure alkohol, are inaccurate.

Alkohol is colourless, and perfectly transparent. Its odour is fragrant, and its taste hot and pungent. It acts powerfully on the animal system, exciting exhilaration and intoxication.

It is always fluid, not congealing even at the lowest cold that has been obtained by artificial methods: it is highly expansible, and is also very volatile. It evaporates quickly, when exposed to the atmosphere: it distils over in close vessels slowly at 100°, and boils at 165°. In this volatilization, it suffers no change but of form, being condensed in its original state. If suddenly exposed, however, to a high temperature, it is decomposed, new combinations being established among its elements. Thus, when transmitted through an ignited tube, it is converted into one or other of the varieties of oxy-carburetted hydrogen gas, according to the temperature, as has been already remarked, (vol. ii. p. 383. 390.). Watery vapour and carbonic acid gas are at the same time formed.

Alkohol is highly inflammable. It kindles when the temperature is not much above 300°, when in contact with atmospheric air, and burns with a blue lambent

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* Nicholson's Journal, 4to, vol. i. p. 110.

flame, without any sensible smoke, and, when pure, without leaving any residuum. It afforded, therefore, to the older chemists the best example of a substance being entirely consumed by combustion. Yet some of them, as Boerhaave, observed, that a quantity of water may be condensed from burning alkohol; and with this, there is also formed a quantity of carbonic acid gas. The quantity of water was found by Lavoisier to amount to about eighteen from sixteen parts of alkohol.

By performing the combustion in vessels adapted to collect the products, Lavoisier endeavoured to infer from this experiment its composition *. Of a quantity of alkohol kindled in a lamp, there were burnt 93.5 grains, and, in the combustion of this quantity, 110.32 grains of oxygen were consumed: there was produced, carbonic acid gas to the amount of 95.28 grains; and a quantity of water was condensed, which Lavoisier calculated to amount to 108.54 grains. From these results, he inferred the composition of alkohol; for, knowing the composition of carbonic acid gas, it was easy to determine, from the quantity of it formed in the experiment, what portion of the oxygen consumed had been spent in its formation, by combining with the carbon of the alkohol; the remaining quantity of oxygen had of course gone to the formation of water, by combining with the hydrogen of the alkohol; and what water appeared over this, Lavoisier supposed to have pre-existed in the alkohol, as essential to its composition. On these grounds, he concluded, that alkohol consists of 28.5 of carbon, 7.8 of hydrogen, and

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* Mémoires de l'Acad. des Sciences, 1784, p. 598,

63.5 of water. But allowing the accuracy of the results, which Lavoisier himself regarded only as approximations, it is obvious, that the inference, that the large quantity of water formed in the combustion above that which could have been derived from the quantity of oxygen consumed, pre-existed in the alkohol, by no means follows, since it might have been rather the elements of this water, or, in other words, the alkohol might contain a portion of oxygen, which would contribute, with the oxygen of the air consumed, to the formation of the water and carbonic acid; and this inference is even more probable, than that so large a quantity of water should exist in alkohol ready formed, combined merely with carbon and hydrogen. Alkohol is probably a ternary compound of these two elements with oxygen. It would be in vain, however, to attempt, from Lavoisier's experiments, to assign the proportions of these, in the uncertainty which at present exists with regard to the proportions of the elements of carbonic acid, and in our ignorance of what is really pure alkohol. The existence of oxygen in its composition may also be inferred, from the products afforded when it is decomposed, by being transmitted through an ignited tube.

Alkohol is capable of combining with water in every proportion. Though, in this case, no new properties are acquired, yet it is a real chemical combination, as is evident from the condensation which always accompanies it. In whatever proportion the two liquors are mixed together, the specific gravity of the compound is never the mean of the specific gravities of the separate fluids, but is always greater. Thus, if one part of alkohol, whose specific gravity is 817, be mixed with one part of water whose specific gravity is 1000, the specific gravity of the compound will not be the mean of their respective gravities, 908.5, but will be not less than 934 ; and a difference will likewise obtain in whatever proportions the fluids are mixed. This difference proceeds in a decreasing ratio ; that is to say, when ten parts of alkohol are mixed with one of water, the difference in the specific gravity which is produced is greater than when the ten parts are mixed with two, and greater in this, again, than when mixed with three. The progression, however, is not regular ; and hence, the specific gravity of any possible mixture of alkohol and water cannot be calculated *à priori,* but must be determined by actual experiment, as has been already remarked.

The greater density which the combination of alkohol with water acquires, is accompanied with a diminution in the capacity for caloric, as has been ascertained by actual experiment ; and hence, a rise of temperature always accompanies their union. In the mixture of pure alkohol with water, this is so considerable as to be perceptible to the hand. Their union is also accompanied with a hissing noise, and the formation of air bubbles. When alkohol is diluted with an equal weight of water, it forms what is named Proof Spirit.

In consequence of its affinity to water, alkohol is capable of precipitating many of the neutral salts from their aqueous solutions. There are others, again, which it does not precipitate, owing to the affinity it exerts towards them, and which, even in its pure state, it is capable of dissolving, particularly those which are deliquescent, which have ammonia, lime, or magnesia for their base ; or the nitric or muriatic acid, for their acid. From both of these properties, alkohol is a very useful re-agent in the analysis of mineral waters, and under the consideration of that subject, will be more fully taken notice of. It has already been remarked, that many of these saline substances give a peculiar tinge to the flame of alkohol in burning.

Alkohol combines with the alkalis. It dissolves potassa and soda in their pure state; and from this property, as has been already remarked, it is employed in their preparation, and enables us to obtain them free from foreign substances. It appears to suffer a decomposition from the alkali, probably from part of its carbon and oxygen being combined by the resulting affinity the alkali exerts, so as to form carbonic acid; for the solution acquires a deep brown colour; and according to Pelletier carbonate of potassa is formed, and the alkohol at length disappears *. Ammonia may likewise be combined with alkohol by distillation. Of the earths, strontites, and perhaps barytes, are dissolved by it.

The acids combine with alkohol, and some of them decompose it; but as a particular order of compounds results from these actions, they will be better considered after the history of alkohol.

Alkohol unites with sulphur, but to effect the combination it is requisite that the sulphur should be presented to it in the state of vapour. In this way their combination was effected by Lauraguais †. According to Favre, however, if alkohol be highly rectified or freed from water, it dissolves sulphur merely by applying heat, though less

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* Mémoires de Chimie, tom. i. p. 321.

† Mémoires de l'Acad. des Sciences, 1758, p. 84.

than sufficient to cause the alkohol to boil. By digesting an ounce of alkohol with two drachms of sulphur, he found from 13 to 23 grains to be dissolved, according to the heat applied *. The compound of sulphur and alkohol formed by the process of Lauraguais, is a liquid of a reddish colour and fœtid smell, resembling that of sulphuretted hydrogen: it becomes turbid on cooling, and sulphur is precipitated from it by the addition of water. The proportion of sulphur it contains is about a sixtieth.

Phosphorus is dissolved by alkohol: the solution is rendered turbid, and the phosphorus precipitated on the affusion of water. When the liquor is poured on water, a tremulous but vivid light is perceived, when the experiment is made in the dark.

Alkohol does not dissolve carbon, nor does it combine with hydrogen. It absorbs, as has been already remarked, nitric and nitrous oxides. It exerts no action on the metals even when they are oxidized, but it dissolves a number of the metallic salts.

Alkohol is the solvent of a number of the vegetable proximate principles, as sugar, resin, extract, camphor, essential oil, and several of the acids. These combinations give rise to various compounds. With essential oils are formed the odoriferous essences and the distilled spirits. These are commonly formed by distillation. A quantity of proof spirit is poured on any aromatic fragrant vegetable: a moderate heat is applied: the alkohol of the proof spirit dissolves the essential oil, and distils over. What are thus formed are named Distilled Spirits, in con-

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* Nicholson's Journal, vol. xiii. p. 70.

tradistinction to Distilled Waters, prepared by distilling water from the plant. As the essential oils are readily soluble in alkohol, the spirit may be easily impregnated with them by agitation.

Camphor dissolved in alkohol forms a compound, which is used in medicine as a stimulant.

Resins dissolved in alkohol, as I have already remarked, form Varnishes. Balsams dissolve in it entirely, gum-resins partially.

Alkohol, from its power of dissolving these principles, is able to extract the active matter of many vegetables; and when diluted with an equal part of water, so as to form proof spirit, its solvent power is still more extensive. Both in its pure and diluted state, it is therefore frequently used in pharmacy to dissolve the active principles of many vegetable products, and thus to separate them from the ligneous fibre or other inert matter with which they may be mixed. Solutions of this kind are named Tinctures or Elixirs. Those that are prepared with pure alkohol are decomposed by water, the resinous matter being precipitated; those with proof spirit, are in general miscible without decomposition.

THE action of the more powerful acids on alkohol, it has been remarked, is peculiar, and gives rise to an order of compounds of some importance from their peculiar properties. These, as produced by the different acids, vary somewhat in their qualities: they also agree, however, in the possession of certain general properties; they are highly volatile, odorous, pungent, and inflammable, miscible with water, and capable of combining with alkohol in every proportion. These compounds are named ETHERS; the specific name of each being derived from the acid, from the action of which on alkohol it has originated, as the sulphuric, nitric, muriatic, or acetic ether.

SULPHURIC ETHER is of these compounds the one which has been longest known. The following is the process by which it is prepared.

Upon a quantity of alkohol in a retort, (selected thin at the bottom, so as to be capable of bearing a sudden heat), is poured an equal weight of sulphuric acid. The acid is added in a full stream, so that from its greater specific gravity it falls at once to the bottom of the retort; it is then mixed with the alkohol above by frequent and moderate agitation. From this mixture the alkohol acquires a brownish colour; vapours having a fragrant odour are disengaged; and the temperature rises to about 180 of Fahrenheit. When the mixture of the acid and alkohol is complete, the retort is to be immediately placed in a sand bath, and connected with two large receivers, which are kept cool, by water or ice. Heat is to be immediately applied to the retort. The liquor boils when the temperature is raised to 208, the ether being formed at that temperature, and distilling over: the condensation of it is to be promoted by keeping the receivers cool with water, and the distillation is to be continued till about half the quantity of the alkohol employed has distilled over, or until the neck of the retort becomes obscured with white fumes, which condense into a matter of apparently an oily consistence.

The liquor which distils over into the receiver is the sulphuric ether. If, to the residual liquor in the retort, there be added half the quantity of alkohol employed in the first distillation, on applying heat, a new production of ether will take place; and this may be repeated for several times.

Towards the end of the distillation, a portion of sulphurous acid is formed and disengaged, with which the ether is so far impregnated, that its fragrance is injured, and its odour rendered pungent and acrid. A portion of water likewise distils over, by which it is diluted. The liquor in the retort, at the end of the distillation, is also found diluted with a portion of water: it is, however, thick, and of a black colour, from a quantity of carbonaceous matter suspended in it.

From the water and sulphurous acid the ether is freed, by subjecting it to a second distillation with a very gentle heat applied by a water-bath, pure potassa being previously added to it, in the proportion of two drachms to each pound; this attracts the sulphurous acid, and renders even the water rather less volatile. Another method of rectification, proposed by Pelletier [*], and revived by Dizé [†], which I have found to succeed extremely well, is to distil the ether of the first distillation from a little black oxide of manganese, the oxygen of which combines with the sulphurous acid, converting it into sulphuric; and this, with the water, remains in the retort. Even after either of these processes, the ether may still contain a portion of alkohol, which usually passes over in the first stage of the distillation. This is best abstracted by agitation with water, which imbibes the alkohol, and a little of the ether: the greater part of the ether floats above, may be drawn off, and, by distilling it with a very gentle heat, is obtained extremely pure.

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[*] Mémoires de Chimie, tom. i. p. 316.

[†] Nicholson's Journal, 4to, vol. iii. p. 43.

A degree of obscurity still prevails with regard to the theory of the formation of sulphuric ether; different views having been entertained of the agency of the acid on the alkohol. The explanation that was generally given, after the establishment of the theory of Lavoisier, was founded on the supposition, that the acid acts principally by communicating oxygen. Alkohol consists of carbon and hydrogen, with a portion of oxygen: when mixed with sulphuric acid, and exposed to heat, it was supposed that part of the acid suffered decomposition, its oxygen being attracted by the hydrogen of the alkohol, and forming water: the balance of attractions between the principles of the alkohol being thus broken, part of its carbon is precipitated, and is diffused through the liquor, rendering it thick and dark coloured; and the remaining quantities of its elements, its carbon, hydrogen, and oxygen, unite and form the ether.

This explanation is founded on the supposition, that the sulphuric acid is decomposed in the process by which ether is formed. But a few years ago it was affirmed by Fourcroy and Vauquelin, from a series of experiments which they undertook to elucidate this subject, that such a decomposition of the acid is not at all necessary to its formation: that although it may take place to a certain extent towards the end of the process when the liquor is loaded with carbon, there is no indication of it in the first stage, during which, principally, the ether is formed; no sulphurous acid gas is discharged, and if the process be stopt at the end of this stage, the remaining acid, they found, is capable of saturating the same quantity of alkali, as before its mixture with the alkohol *.

These chemists gave, therefore, a different view of this subject, which they applied even to the action of this acid on vegetable matter in general. They suppose, that the sulphuric acid suffers no decomposition, and that it acts no other part than causing, by the exertion of a disposing affinity, the decomposition of the alkohol. By this affinity it disposes part of the hydrogen and of the oxygen of the alkohol to combine and form water: the balance of attractions being thus subverted, a quantity of carbon is separated, and the remaining carbon, hydrogen, and oxygen, combine and form the ether.

This theory, however, advanced by these chemists, is not perhaps perfectly established. Though they affirm, that the acid remaining after the formation of ether, saturates as much alkali as it would do previous to its mixture with the alkohol, the experiment by which this is supposed to be established, is not altogether without fallacy. During the formation of ether, there is always also a formation from the elements of the alkohol, of some of the vegetable acids, particularly of the acetous and oxalic. The oxalic, it has been acertained by the observation of Cadet, is formed copiously even without heat, merely by allowing the mixture of acid and alkohol to remain at rest for some time. These will contribute to the saturation

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* Nicholson's Journal, 4to, vol. i. p. 385.

of the alkali; so that if none of the sulphuric acid were decomposed, more alkali ought in reality to be saturated by it after, than before its mixture with the alkohol.

There are also some facts which appear to prove the necessity of the presence of some substance that can part with its oxygen, for the production of ether. Thus, ether cannot be formed from the muriatic acid, but it can with facility from the oxymuriatic: it is likewise formed with great rapidity by the nitric acid; neither of which can exert a strong disposing affinity to water, though both very readily part with their oxygen.

From these facts it is evident, that it is at least still doubtful but that the decomposition of the acid, and its affording oxygen, is necessary for the formation of ether. The quantity of sulphurous acid that may be produced from this decomposition, may be retained by the ether, as it is capable of combining with it; may enter into combination with its elements; or what is most probable, may be retained by the sulphuric acid.

Laudet and Dabit published some experiments* in opposition to the theory of Vauquelin, in which it appeared to be proved, that ether is formed when alkohol and black oxide of manganese are mixed and exposed to the proper heat, a very small quantity of sulphuric acid (as an ounce to a pound of alkohol) being added, merely to favour their action; and that muriatic acid heated with alkohol, gave no ether; while, if black oxide of manganese were added, an ether was formed: whence they inferred, that the communication of oxygen is necessary to the formation of ether. In opposition to these, Fourcroy and Vauquelin affirmed, that the liquors thus formed differed from ether in their constitution and properties *: but admitting this, they appear to approach to it; and the facts above stated still remain unfavourable to the theory of these chemists.

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* Annales de Chimie, tom. xxxiv. p. 282. 289.

Whatever opinion, however, may be formed as to the manner in which the changes that take place during the formation of ether are produced, the nature of the changes themselves seems sufficiently well ascertained. It is proved, that a quantity of the hydrogen of the alkohol is expended in the formation of water, as the remaining acid is always in a diluted state : a still larger quantity of carbon is also separated, and is mechanically diffused through the liquor. The ether, therefore, which is the only other product of the operation, is to be considered as a compound of hydrogen and carbon, and perhaps oxygen; differing from alkohol in containing a much larger quantity of hydrogen proportioned to its carbon; and to this predominance of hydrogen its great levity and volatility are owing. This conclusion is confirmed, by its analysis by combustion, the products of which are water and carbonic acid; the former being derived from the combination of its hydrogen with the oxygen of the air, the latter from the same combination of its carbon. Mr Cruickshank found, that the vapour of ether requires about seven times its volume of oxygen to saturate it in combustion; the products being water and carbonic acid gas, the latter amounting to 4.6 parts by measure. From this result, compared with a similar experiment on alkohol, he infer-

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* Annales de Chimie, tom. xxxiv. p. 318.

red, that the proportion of carbon to hydrogen in the ether, is as 5 to 1 nearly, while in alkohol it is as 8 or 9 to 1 *.

Besides ether, there are some other products formed during the action of sulphuric acid upon alkohol. Towards the end of the process an oily-like matter distils over, which has been named Sweet Oil of Wine. This can be obtained separate, by changing the receiver: it is unctuous, thick, and less volatile than the ether, but is soluble both in it and in alkohol. It is obtained likewise by distilling sulphuric ether from a fresh quantity of acid. Chemists are not agreed respecting its nature: Fourcroy and Vauquelin consider it as similar to ether, and that it differs from that fluid principally in containing a larger proportion of carbon, which gives to it more density and less volatility. Other chemists, particularly Higgins, have affirmed, that it is a compound of ether and sulphurous acid, and that by the addition of an alkali which combines with the acid, a quantity of ether may be obtained from it. It does not appear, however, that this combination can be formed directly, or that ether can combine with a large quantity of sulphurous acid, so as to assume the properties of oil of wine; and though this substance may contain a portion of this acid, it is not improbable that it also differs from ether in its ultimate composition.

At the same time that the oil of wine is disengaged, there is formed a quantity of olefiant gas, which passes off. It was in this process indeed, that the production of this gas was first observed; and the action of sulphuric acid on alkohol still affords us the best method of obtain-

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* Nicholson's Journal, 4to, vol. v. p. 205.

ing it pure. The same gas is produced, by passing the vapour of ether through an ignited earthen tube; but, when a glass tube is used, a different variety of carburetted hydrogen is obtained, as has been already stated, (vol. ii. p. 390).

At this stage of the process the liquor becomes so loaded with carbon, and at the same time is capable of bearing so high a temperature, that if the heat is kept up, the sulphuric acid is decomposed, and a large quantity of sulphureous acid gas and carbonic acid is produced. If the greatest care is not taken to keep the heat moderate, the whole liquor is apt to swell suddenly up, and boil over into the receiver. If examined at this time, it is likewise found to contain a portion of acetic and oxalic acids mixed with the sulphuric acid, which is diluted with water, and through which the carbon is diffused.

It remains to take notice of the properties of Sulphuric Ether.

When highly rectified, it is the lightest of all known liquids. It is obtained without difficulty of the specific gravity of .732, and by careful distillation has been brought so low as .716. It is colourless and perfectly transparent; has a strong pungent taste, and a fragrant penetrating smell.

It is likewise the most volatile liquid. It evaporates rapidly even at the common temperature, and under the common pressure of the atmosphere; so that it cannot be poured from one vessel into another without loss, and any part wet with it immediately becomes dry. In vacuo it boils at a temperature considerably below 32°: under the atmospheric pressure it boils at 98. In the spontaneous evaporation of ether, a large quantity of caloric is absorbed, so as to produce cold: water inclosed in a small tube may be easily frozen, by ether evaporating from a piece of muslin wrapt round the external surface of the tube; and Dr Higgins has observed, that in the rapid evaporation of ether, the temperature in frosty weather falls so low as —40. Ether congeals at —47.

From this volatility of ether it almost immediately enlarges the volume of any elastic fluid into which it is dropt; the volume at a common natural temperature being doubled according to the observation of Priestley, who also observed, that the etherial vapour in this case could not be condensed by cold, but was absorbed by water.

Ether is highly inflammable, and, when kindled, burns with a clear white flame, without any smoke, and without leaving any residuum, the products of its combustion being water and carbonic acid: the residual water generally gives indications, too, of sulphuric acid, which may either be adventitious, or perhaps is essential to the constitution of this species of ether. From its high inflammability, its vapour diffused in the atmosphere sometimes takes fire; or if a drop or two of ether be added to atmospheric air or oxygen gas, an explosion happens, on the contact of an ignited body. Mr Cruickshank found, that by agitating a little oxygen gas with sulphuric ether, the volume was exactly doubled: in this state, it did not explode; but when one part of it was added to three parts of oxygen, "an ignited body, or the electric spark, then produces a dreadful explosion *." It is also kindled by

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* Nicholson's Journal, 4to, vol. v. p. 205.

hyper-oxymuriatic acid gas. Mr Cruickshank relates a striking experiment from this combustion. If a bottle of the capacity of three or four pints be filled with this gas, taking care to expel the water completely, and there be thrown into it about a drachm of ether, covering the mouth of the bottle immediately with a piece of paper, in a few seconds, a white vapour is perceived moving circularly in the vessel, which is soon followed by an explosion, accompanied with flame. A considerable quantity of carbon is at the same time deposited.

Sulphuric ether is soluble in water, but only in a limited proportion. When highly rectified, it requires ten parts of water for its solution; and this is a property by which we are enabled to determine its purity, as, if more soluble, it contains either water or alkohol. It is soluble in alkohol in every proportion.

Sulphuric ether exerts no sensible action on the fixed alkalis or earths. It unites with ammonia by distillation.

Neither does it act on the metals; but it is capable of decomposing the saline combinations of those that have a weak affinity to oxygen, by attracting that principle. Thus, muriate of gold dissolved in it is gradually decomposed, and the gold precipitated in its metallic form.

On the simple inflammables, its action is somewhat similar to that of alkohol. It dissolves sulphur, as Favre has shown, one ounce of ether dissolving about twenty-five grains: the solution has a strong sulphurous smell and taste: it is less soluble in water than pure ether, and deposites sulphur as the ether volatilizes*. Ether likewise dissolves a small proportion of phosphorus: this solution, like the phosphuretted alkohol, is decomposed by water, but does not, like it, appear luminous during the decomposition.

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* Nicholson's Journal, vol. xiii. p. 69.

Sulphuric ether is a solvent of many of the vegetable proximate principles, as the essential oils, camphor and resins. It is also, as has already been remarked, the most powerful solvent of caoutchouc.

In medicine, it is employed as a diffusible stimulant.

Nitric Ether. The action of nitric acid on alkohol is so violent, that the formation of nitric ether is extremely difficult, and requires considerable precaution. One part of the acid may be added gradually to three parts of alkohol without any risk; and after standing for some days, to allow of their reciprocal action, heat may be applied, when a portion of nitric ether that has been formed distils over, with a quantity of unchanged alkohol. A preparation of this kind has been long known in pharmacy, under the name of Sweet Spirit of Nitre. But when the proportion of acid is increased, the action becomes very violent; a quantity of aërial fluid is suddenly formed, and disengaged at each addition; and it requires particular arrangements to admit of so much acid being added as is sufficient to convert the whole of the alkohol into ether.

The method proposed by Navier is, to put into a strong earthen-ware bottle twelve parts of alkohol, and immerse it in water or ice; eight parts of nitrous acid are to be added in successive portions, mixing them by agitation at each addition; the bottle is well corked, and tied over, and is put in a cool place. At the end of six days, the cork is to be perforated, to allow a quantity of aërial fluid that has been formed, and is retained by compression, to escape. The bottle is then uncorked, the liquid poured into a funnel, and the acid liquor beneath allowed to run off from the ether which swims above.

An ingenious method, somewhat similar, but less hazardous, was employed by Dr Black. He first poured into a strong flint-glass bottle six ounces of alkohol; then, by a funnel, the tube of which reached to the bottom of the bottle, he poured in two ounces of water gently, so that it did not mix with the alkohol, but raised it above it; and, lastly, he poured in four ounces of nitrous acid in the same manner, so that the small column of water was interposed between it and the alkohol. The phial was set aside for some time in a cool place: the water attracted the alkohol at the one surface, the acid at the other, and thus brought them very gradually together, so as to admit of their reciprocal action without violence. At the end of a few months they were completely mixed, and nitric ether formed, which floated above, was withdrawn, and rectified by distillation.

Various other methods have been employed. The process of Woulfe consists in connecting a high-necked tubulated retort or matrass with a large globular receiver, which is connected by a tube with a range of tubulated bottles, in which water or alkohol is put; eight ounces of alkohol are poured into the retort, and six ounces of nitrous acid are added in successive portions. At each addition, after a certain quantity of the acid has been added, there is a disengagement of gas. At the end of the operation a quantity of nitric ether [illegible] found to have been formed and volatilized by the heat produced by the mutual action of the acid and alkohol : it is collected in the globular receiver, or in a bottle connected with it, is removed, and may be rectified by mixing it with water, and afterwards distilling it. The alkohol in the receivers contains a portion of it also, and may be employed in a repetition of the process; and the residual liquor in the retort contains also alkohol impregnated with ether. Woulfe afterwards modified his process, by using alkohol, nitre and sulphuric acid, four pounds of nitre being put into the retort, and a mixture of 4 ℔s of sulphuric acid, and 3 lbs. 5 ounces of alkohol being added to it, in quantities not exceeding two ounces at a time, and only after the disengagement of elastic fluid from the previous addition has ceased. Pelletier has observed, that after repeating all the processes known to him for the preparation of nitric ether, he found this to succeed best; nor could he discover in the product of it the most minute portion of sulphuric acid *.

The theory of the formation of nitric ether is as obscure as that of sulphuric ether. It is ascertained, however, that even from the commencement of the process the acid is decomposed; nitric oxide gas is disengaged; and Pelletier found even that in following the process of Woulfe, the decomposition was complete, nitric acid not being discoverable, either in the liquor which passed over, or in the residuum.

This appears, too, very clearly from some experiments

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* Mémoires de Chimie, tom. i. p. 99.

by Bayen. He ascertained what quantity of carbonate of potassa was necessary to saturate a certain quantity of nitric acid; one ounce required 282 grains. He then digested one part of acid with two of alkohol, for five weeks, and at the end of this time he found the liquor was not capable of saturating half the quantity, that the acid previous to its mixture would have done; three ounces of it containing one ounce of acid, saturating only 134 grains of the carbonate, so that even without the application of heat, much of the acid had been decomposed. He then repeated the experiment, applying heat, and after distillation mixing the product and residual liquor together, and found that three ounces of it saturated only 32 grains. And as a quantity of oxalic acid is formed in the process, it is probable that it principally had produced this effect; so that in this case the whole of the nitric acid had suffered decomposition *.

It is also proved, that in the formation of nitric ether, the alkohol suffers decomposition, as in the residual liquor oxalic and acetic acids are formed. There is no deposition, however, of carbonaceous matter, as there is in the formation of sulphuric ether, the residual liquor being quite transparent, and of a light colour. It appears to follow, therefore, from these facts, that in the formation of nitric ether, part of the elements of the alkohol combine with oxygen from the nitric acid, and form oxalic and acetic acids; carbonic acid gas too, is formed and disengaged, as Pelletier found, in considerable quantity, and much of the nitric acid mixed with nitric oxide and ni-

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* Opuscles Chimique, tom. i. p. 384.

trogen gases *. It is difficult, however, to determine in what manner these facts are to be combined, so as to give with precision the theory of the formation of nitric ether: nor is it very apparent, whether any of the elements of the nitric acid enter into its composition, or whether they are entirely disengaged during the process. It might be supposed, that it must contain more carbon than sulphuric ether, as none is deposited during its formation; but we are not certain what quantity is carried off in the state of carbonic acid.

Nitric ether has some resemblance in its properties to sulphuric ether. Like it, it is light and volatile, and has been said, when highly rectified, to have these qualities even in a higher degree than sulphuric ether. It is also inflammable, burns with an enlarged flame, and is said to deposite more charcoal. It is soluble in water and in alkohol. Its odour is strong, though scarcely so agreeable as that of sulphuric ether; in the state, however, of what has been named Dulcified Spirit of Nitre, it is more fragrant. Its colour is usually yellow; but this, as well, probably, as some of its other qualities, appears rather to be owing to the presence of nitric acid, surcharged, perhaps, with nitric oxide. Thus, when kept, it continues to emit an elastic fluid, and tinges the cork of the phial yellow or red; and Deyeux found, that when one part of it is mixed with sixteen parts of water in a bottle with a tube, the nitric gas which it contains is separated from it by a spontaneous effervescence: after this, it ceases to emit gas on keeping. Another proof of the presence of

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* Mémoires de Chimie, tom. i. p. 138.

nitric acid or oxide in it is, that when kept a long time, crystals of oxalic acid are formed and deposited. Deyeux found, that it is rendered colourless by distilling it from the alkalis, or from sugar, which appears to be oxidized by this distillation *. It is only as thus rectified that it can be regarded as pure; but in this state its properties have scarcely been examined.

The residuum of nitric ether is transparent, of a yellow colour: its smell, as Fourcroy has remarked, is aromatic, and its taste acid and pungent. When distilled, it affords a fragrant acidulous liquor; and what remains in the retort deposites crystals of oxalic acid.

When equal parts of nitric acid and alkohol are mixed together, a strong effervescence soon takes place, and a gas is disengaged, which is slowly absorbed by water, explodes when mixed with oxygen and kindled, and is decomposed by sulphuric, nitric, and muriatic acids, which disengage from it nitric oxide gas. It has been named Nitrous Etherized Gas by the Dutch chemists, who first took notice of it, and appears to be a compound of nitric ether and nitric oxide gas.

MURIATIC ETHER. Chemists always found it impracticable to form an ether by the action of muriatic acid on alkohol, in whatever state of concentration they used it. By using, however, the acid in a state of combination with metallic oxides, from which a portion of oxygen might be derived, they succeeded more or less completely in forming a species of muriatic ether, as by the medium of the

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* Annales de Chimie, tom. xxii. p. 144.

muriate of antimony, tin, or zinc distilled with alkohol. Prior to the discovery of oxymuriatic acid, the rationale of these operations, however, was not understood. No sooner had this discovery been made by Scheele, than he availed himself of it to attempt the formation of muriatic ether, by distilling muriatic acid from black oxide of manganese, receiving the gas in alkohol, and afterwards rectifying this liquid by distillation with a very gentle heat.

The success of this process, however, Scheele found to be imperfect; and the product approached rather to an oil in appearance than a light ether. And Berthollet found, that though, by passing a current of oxymuriatic acid gas through alkohol, it was absorbed rapidly, and passed to the state of muriatic acid, while the alkohol acquired an odour of ether, which became stronger on a repetition of the process; yet, on repeating it a third and fourth time, this odour diminished, and at length was nearly entirely lost, the liquor having rather the smell of vinegar; and on distilling it, after a small quantity of etherial liquor passed over, there was obtained only a watery liquor, which had the odour of burnt sugar; the residuum had the same odour, and even the taste of this substance very strong, and contained a quantity of acetic acid *. This result, it may be remarked, is a singular one, as apparently proving the reproduction of sugar from alkohol.

Scheele had also distilled together muriate of soda, black oxide of manganese, sulphuric acid, and alkohol, to produce muriatic ether; and this process was after-

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* Mémoires de l'Acad. des Sciences, 1785, p. 309.

wards employed by Pelletier. He introduced into a tubulated retort a mixture of eight ounces of black oxide of manganese, and a pound and a half of muriate of soda, on which was poured a mixture of twelve ounces of sulphuric acid and eight ounces of alkohol. On applying heat, a liquor was obtained highly etherial, weighing ten ounces, from which, by rectification, four ounces of ether were procured *.

Pelletier observed, that, in this rectification, when the alkali is added, an effervescence takes place, and an oily matter separated in large quantity, which remained floating on the residual liquor. According to Van Mons, this oil is produced by the action of the oxymuriatic acid on the muriatic ether; and from this circumstance, it is scarcely possible, he affirms, by the process of Scheele and Pelletier, to obtain that ether in any quantity. It at first floats on the surface of the water; but, if not soon separated, or when submitted to rectification, it is converted into this oil, which gradually becomes thick, from the continued action of the acid. And when ether appears to have been formed by the process of Pelletier, he supposes that it has been sulphuric ether, somewhat disguised by intermixture of the other products.

He therefore proposes the following process to form muriatic ether: Place a retort in a sand-bath, and connect it with a glass balloon, and two of Woolfe's bottles: put into the bottle 100 parts of muriate of soda perfectly dry, and into the balloon and bottles the same quantity of alkohol. The joinings being luted, 50 parts of sul-

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* Mémoires de Chimie, tom. i. p. 142.

phuric acid are to be poured on the salt, and the operation is left to proceed in the cold for five or six hours. A moderate heat is then to be gradually applied. The muriatic acid gas passes over, and is condensed by the alkohol. The whole of this liquor is then put into a retort, with 20 parts of oxide of manganese in fine powder; and there is put into the receiver and bottles a solution of pure potassa. It is distilled with a gentle heat: the muriatic ether passes over, and the re-action of any excess of oxy-muriatic acid gas upon it, which would change it to oil, is prevented by the alkali. The ether is then to be rectified, by mixing it with twice its bulk of water, and distilling it by a very gentle heat *.

Mr Bossa likewise observed, that, by the usual process with oxymuriatic acid, a muriatic ether could never be formed, but only a heavy oily fluid: And he has affirmed, that it may be formed from muriatic acid. His process is to pass a current of muriatic acid gas from 20 ounces of perfectly dry muriate of soda, and 10 ounces of sulphuric acid, gradually mixed, in a retort, through 10 ounces of highly rectified alkohol, placed in a bottle with two necks, kept cool. The alkohol thus charged with acid is distilled to one half: the distilled liquor is to be agitated with an alkaline solution, to remove any superfluous acid; and the liquid which floats above is the muriatic ether †. The result of this process is in opposition with the experience of former chemists, who were always unable to form an ether with muriatic acid.

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* Philosophical Magazine, vol. vii. p. 48.

† Nicholson's Journal, vol. v. p. 221.

The properties of muriatic ether have not been properly described, from the difficulty of obtaining it pure. It is said to be light, transparent, and volatile, inflammable, emitting, while burning, a pungent odour, and to have a styptic taste.

A process has been given by Boudet for the preparation of PHOSPHORIC ETHER. He mixed liquid phosphoric acid of a thick consistence and alkohol in equal proportions, introduced the mixture into a tubulated retort connected with a receiver, and with an Woolfe's bottle, which was filled two-thirds with lime-water: heat was applied, so as to cause the mixture to boil; a portion of unchanged alkohol first distilled over; this was succeeded by a liquor having an etherial odour, mixed a little with that of garlic: it reddened slightly the syrup of violets: when rectified by distillation, with the addition of carbonate of magnesia, the product was colourless, and had an odour somewhat similar to that of sulphuric ether: it was volatile, and highly inflammable, its combustion not being accompanied with any smoke. It floated on the surface of water, but, by agitation with it, was dissolved. It dissolved the volatile oils, and also phosphorus. Its specific gravity was inferior to that of alkohol, being as 94 to 100. After its production, when the heat was much raised, a quantity of oily matter was distilled over, and carburetted hydrogen was disengaged. The residual liquor was of a dark brown colour, and contained a large quantity of phosphoric acid *.

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* Annales de Chimie, tom. xl. p. 123.

FLUORIC ETHER has been said to be formed by putting fluate of lime, previously ignited and in powder, into a retort, with equal weights of alkohol and sulphuric acid, and distilling to dryness. The product of this distillation was again distilled to one half, and a portion of fluoric acid abstracted from it by a solution of potassa, which, at the same time, precipitated a portion of silex, so as to render the whole gelatinous. This, on being again distilled, afforded an ether of the specific gravity of 0.720, which burnt with a blue flame, and had a bitter taste. It is added, that it greatly resembled sulphuric ether; and it is not improbable, that it may have been merely this ether disguised *.

ACETIC ETHER has been known for a considerable time to chemists, Lauragais having given in 1759 the process for preparing it, by distilling alkohol, with the concentrated acetic acid that is procured by the decomposition of acetate of copper by heat. Scheele, as well as other chemists, have been unable to form it; but Pelletier has observed, that it is procured with certainty, by distilling alkohol repeatedly from the acetic acid. The alkohol at first acquires an etherial odour, but is miscible with water; by returning it on the residual liquor, distilling it, and repeating this for a third time, this becomes stronger: the acid contained in the liquor thus procured was saturated by the addition of carbonate of potassa; and, by distillation, there was procured from it a pure acetic ether, in quantity about half of the alkohol employed †. It was soluble in water

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* Nicholson's Journal, vol. viii. p. 143.

† Mémoires de Chimie, tom. i. p. 237.

in limited quantity, seven measures dissolving three. It has an agreeable odour, etherial, but in which the smell of acetic acid is also perceptible. It is very volatile and inflammable : it burns with a clear light, and leaves a little charcoal.

According to Pelletier, acetic ether may likewise be formed by distillation, from a mixture of sulphuric acid, acetate of copper, and alkohol; and, according to Laplanche, it may be obtained from a mixture of sulphuric acid, alkohol, and acetate of lead.

To the vinous fermentation probably belongs that kind of fermentation which takes place in the raising of bread. A small quantity of yeast is mixed with the flour; or, without this addition, a quantity of the flour of wheat is mixed with hot water, allowed to stand for a day or two, and is then used as a ferment. A portion of it, or of the yeast, is mixed with flour into a soft paste, and is kept in a warm place: it swells up, becomes spongy, from the extrication of a quantity of air, and, were the fermentation allowed to continue, would become sour. A small quantity of this leaven, as it is named, is mixed with the dough from which the bread is to be baked: a degree of fermentation is thus excited, and the gas extricated raises the dough. It is soon checked by the baking; but its effects remain, and give rise to the sponginess, porosity, and consequent lightness of well-baked bread. The bread fermented with yeast is less liable to become sour than where the ferment from flour merely is used.

Though some chemists have considered this as a peculiar species of fermentation, there can be no doubt, that it is perfectly analogous to the vinous. Dr Pennington had denied this, from finding, that, on submitting dough to the action of yeast for three quarters of an hour, and then subjecting it to distillation, it gave merely water, without any spirit. But, as Mr Collier very justly remarked, this can only prove, that a complete fermentation is not necessary to raise bread. It is easy to conceive, that it may proceed a certain length, so as to produce that effect, by the extrication of carbonic acid, and yet not fully convert the fecula of the flour into alkohol. And Mr Collier found, that, on subjecting wort for the same length of time to the action of yeast, though it exhibited every sign of fermentation, it gave no spirit by distillation *. That it is the vinous fermentation which happens in the raising of bread from the action of the ferment on the flour, is also sufficiently proved by the fact, that, if not checked, it soon runs into the next stage of fermentation, the acetous, as is evident from the bread becoming sour, and from its peculiar smell in this state. And in suffering this change, it consumes, according to Saussure †, a portion of the oxygen of the air, in the formation of carbonic acid, which is precisely the chemical action that takes place in the acetous fermentation.

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* Manchester Memoirs, vol. v. p. 255.

† Recherches Chimiques, p. 146.

SECT. II.

OF THE ACETOUS FERMENTATION.

If liquors which have undergone the vinous fermentation be kept at a temperature not much below 60°, and with the air not entirely excluded, they gradually suffer another change; they lose their vinous flavour, pungency, and intoxicating quality, and become more or less sour. Chemists have considered this as a second stage in the general process of fermentation; have named it the Acetous; and the product forms Vinegar or Acetic Acid.

Not only do vinous liquors suffer this change, but every substance susceptible of the vinous can likewise pass into the acetous fermentation. Hence, sugar dissolved in water, sweet vegetable juices, or infusions of grains that have been malted, can be converted into vinegar. Fecula, even without the previous process of malting, is equally susceptible of it; for, in the process of starch-making, a quantity of vinegar is formed, not merely from the small portion of saccharine matter in the grain, but likewise, as Vauquelin, in his analysis of the sour liquors of the starch-makers, has remarked, from the fecula itself [*]. Even substances which are not at all susceptible of the vinous fermentation, it appears to be established, may suffer the acetous. This is indeed contrary to an opinion formerly maintained, which regarded the acetous merely as a continuance of the vinous fermentation, and as necessarily preceded by it. But it often happens where the former cannot be traced, and where there is no reason to suppose that it ever did exist, as in vegetable juices or infusions containing much mucilaginous with scarcely any saccharine matter, which soon become sour; and the sourness which even pure mucilage, or a solution of gum in water suffers, is probably owing chiefly to the production of acetous acid.

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[*] Annales de Chimie, tom. xxxviii. p. 261.

Nor is pure alkohol, in any state of dilution with water, capable of undergoing the acetous fermentation: there must always be present other vegetable principles, as sugar, mucilage or farinaceous matter. Even a certain proportion of these is requisite. Hence strong wines do not become so readily sour as weak or sweet wines; for the same reason wine that has been clarified is less liable to ferment; and strong wines can be made to pass into the acetous fermentation more easily, by adding to them sugar or mucilage; and when these highly spirituous wines are thus made to ferment, they furnish a much stronger vinegar than those which are weak. Even the vegetable acids appear to contribute to it, and in the conversion of sweet vegetable juices or of wine into vinegar, there is reason to believe that the malic and tartaric acids they contain are partly changed and pass into the acetic acid.

The addition of some substances which act as ferments, appears also to be requisite. It is true, that wine and other fermented liquors will of themselves become sour in a certain time; but this is probably from their containing a portion of matter analogous to ferments, and which excites the change. In preparing vinegar, it is known that a certain quantity of such matter must be added, either a portion of the substance which has been deposited from a liquor that has previously passed into vinegar, or a quantity of yeast; and there is every reason to believe, that it is vegetable gluten which is the essential principle of these ferments. Fourcroy and Vauquelin accordingly found, that when sugar was added to water which had stood over the gluten of wheat, it quickly formed vinegar; and Berthollet obtained the same result from a mixture of gluten and starch *. This principle Vauquelin remarks contributes to the formation of vinegar in the liquor formed in the manufacture of starch; and the matter which is contained in common vinegar from malted grain, and which renders it so liable to a kind of putrefaction, is, according to this chemist, vegetable gluten.

The admission of the atmospheric air is essential to the acetous fermentation. Hence wines that are well bottled may be kept for a long time uninjured, and the more free the exposure to the air is they become sooner sour. The oxygen of the air is at the same time always absorbed. According to Saussure, this oxygen is not absorbed so as to enter into the composition of the acid, but is expended entirely in abstracting carbon, and of course forming carbonic acid. In keeping wine in contact with oxygen gas for a year in receivers closed with mercury, he found it converted into vinegar; but the diminution of the volume of the gas never exceeded, but was always inferior to the volume of the wine; and hence, according to the view he gives of the experiment, the oxygen had combined with carbon so as to form carbonic acid,

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* Annales du Museum National, tom. vii.

which had been absorbed by the liquor. And accordingly he found, that when he made the experiment with wine previously impregnated with carbonic acid gas, this wine, under the same circumstances, was equally converted into vinegar, but without the volume of the elastic fluid above it being changed; the oxygen consumed being replaced by an equal volume of carbonic acid gas *.

A certain degree of temperature is requisite to the acetous fermentation. It takes place slowly, even below 60; but it proceeds with more rapidity between 60 and 80; and in forming vinegar artificially the temperature is kept high. If it fall below 50, it is nearly checked; and hence wines can be longer preserved by being kept below this temperature.

The phenomena which occur in the acetous fermentation are somewhat analogous to those in the vinous. When it is proceeding rapidly, there is an intestine motion, not accompanied however with such a disengagement of elastic fluid as in the vinous fermentation; the liquor is turbid, and its temperature rises; its smell becomes perceptibly acetous. These appearances at length subside, and the liquor gradually becomes clear, having deposited a kind of glutinous sediment somewhat similar to yeast.

The theory of the acetous fermentation is not yet completely elucidated. Since the strength of the acid which is formed from it is proportioned to the quantity of alkohol, or of matter of a composition analogous to alkohol and in general capable of passing into it, and since this

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* Recherches Chimiques, p. 144.

alkohol disappears during the fermentation, Lavoisier supposed that the theory of the process might be inferred from the changes which this principle can be supposed to suffer; and, as he found that during the change oxygen is absorbed, while scarcely any sensible quantity of carbonic acid is extricated, he concluded, that the acetous fermentation consists in the oxygenizement of the alkohol. If the experiments of Saussure be admitted as correct in proving that as much carbonic acid is formed as corresponds with the quantity of oxygen consumed, this acid being retained by the liquor, the theory of Lavoisier would require to be so far modified, as to ascribe the change of alkohol into vinegar rather to the abstraction of carbon than the fixation of oxygen; leaving of course, however, a larger proportion of the latter principle in the composition of the acetic acid.

This simple view cannot however be received as altogether just, since alkohol alone cannot undergo this change, nor can it by oxygenizement be converted into acetic acid; and since the presence of mucilage, saccharine matter, or other principles, is always necessary to the acetous fermentation, the operation of which is not explained in conformity to this theory. Neither does it explain the action of the ferment which appears to be nearly equally indispensable. It will afterwards appear, that nitrogen probably enters into the composition of acetic acid; and the operation of the ferment may be partly that of affording this element.

Vinegar, the product of the acetous fermentation, is prepared in different countries from different materials. Where the grape is cultivated, it is obtained from weak or spoilt wine. This is kept in a proper temperature with the access of the air, and the fermentation is excited by the addition of a quantity of the sediment of vinegar, of wine already sour, or of the lees of such wine. The product is stronger in proportion to the previous strength of the wine. In this country it is prepared either from unrefined sugar, or from the wort obtained by infusion from malted grain; the fermentation being excited by yeast, and being carried on in a warm apartment. This vinegar is in general inferior in strength and purity to that from wine, and is more liable to become mouldy, or suffer the putrefactive fermentation. This appears to be owing chiefly to the presence of glutinous matter; and hence the rationale of the method which Scheele pointed out as the best for preserving vinegar, that of heating it, and bringing it even to boil for a few minutes, the glutinous matter being separated by a kind of coagulation.

Vinegar, when fully fermented, is clear and limpid, of a yellow or reddish colour, having an odour agreeable and somewhat pungent, and a taste sour but not disagreeable. It differs, however, in its strength and purity as prepared from different materials. It is always very largely diluted, or the acid which is its essential part is combined with a large quantity of water; and with this are in solution portions of gluten, mucilage, sugar, and extractive matter, from which it derives colour, and frequently some of the vegetable acids, particularly the malic and tartaric. It is in this state, as prepared by fermentation, that it is used as a condiment.

The acid which exists in vinegar, is also formed in other chemical processes than fermentation. Thus it is produced spontaneously, as has been already remarked, in the liquor in which wheat is macerated in the formation of starch: it appears frequently in cases where vegetable matter has been acted on by sulphuric, nitric, or oxymuriatic acid, as in the preparation of ether, and in a number of analogous operations; and it is produced in the decomposition of many vegetable substances by heat, constituting what the chemists formerly named the Empyreumatic Vegetable Acids. It also exists ready formed in the sap of many vegetables, as has been already stated.

From vinegar it is procured with most facility, and different processes are followed to obtain it pure and concentrated. The simplest method of obtaining it pure, though weak, is by distillation. A quantity of common vinegar is distilled in a retort with a sand heat, or in a tin still with the fuel directly applied. The first portion that passes over to the amount of about $\frac{1}{8}$ of the vinegar, is little more than water, and is therefore rejected: what passes next is acid, and forms the distilled vinegar. When about $\frac{2}{3}$ have been distilled, the residual liquor becomes so loaded with extractive matter, and at the same time requires so high a temperature to keep up its ebullition, that were the distillation continued it would be scorched, and the distilled liquor would acquire a very unpleasant empyreumatic odour. It is therefore stopt. The residual liquor, however, is still strongly acid, even more so, indeed, than what has passed over. If the receiver be changed, this strong acid may be distilled, and can be applied to some uses; or by adding to the residual liquor a portion of water, the distillation may be recommenced, and a fluid similar to what has before been collected be obtained. At the very end of the operation, when it has been carried on without dilution, there remains a liquor of a deep red colour, very empyreumatic, acid, and which on standing deposites super-tartrate of potassa. The extractive matter, when urged with a strong fire, yields the usual products of vegetable matter, with a portion of ammonia.

Distilled vinegar is limpid and colourless. Its odour is fainter and less pleasant than that of common vinegar; its taste less sour, and its acid powers, as may be inferred indeed from what has been said of its preparation, are weaker. It is purer, however, and is not liable to decomposition on keeping. It is principally used in pharmacy.

Vinegar can be concentrated by freezing: the congelation takes place at a temperature below 28°, more or less according to its strength, and the congealed part is merely ice, leaving of course a stronger acid. If the process be performed on distilled vinegar, or conducted in the manner described by Lowitz, a very pure acid is at the same time obtained. He freezes a large quantity of vinegar, and distils the unfrozen part in a water-bath; the distilled vinegar thus procured, is again congealed, and the liquid portion is lastly distilled from a quantity of charcoal powder. A highly concentrated acid, of an agreeable odour, is thus obtained. If it be exposed to a very intense cold, equal to —38°, it shoots into crystals; when the fluid part is withdrawn, the crystals liquefy when the temperature rises, and the liquid is limpid as water, extremely strong, and has a highly pungent acetous odour. This is the pure acid of the vinegar, any foreign matter remaining in the uncongealed liquid. Lowitz likewise obtained the acid equally strong, by taking vinegar which has been once congealed and then distilled, mixing it with a large quantity of charcoal powder, and distilling from a retort in a water-bath; a weak acid comes over: the retort is then to be placed in a sand-bath, and urged with a strong fire, as long as any fluid distils over quickly; stopping it when it begins to distil more slowly, as it is then principally water. The distilled acid may then be further concentrated by freezing, retaining the crystals, and pouring off the uncongealed portion *. It is singular, that the acid concentrated by freezing, acquires an unpleasant odour; from which, however, it may be freed by distillation from charcoal.

Other methods are likewise employed, to obtain the pure and concentrated acid. Distilled vinegar is combined with an alkali or earth; the neutral salt, obtained by evaporation or crystallization, in a solid state, is decomposed by an acid, and the acetic acid is distilled. The process of Westendorf, which has been often followed, is to saturate soda with distilled vinegar; obtain the acetate by crystallization; and pour upon it, in a retort, half its weight of sulphuric acid. By applying heat, the acetic acid is distilled over; and should there be any reason to suspect the presence of any sulphuric acid, it may be distilled a second time from a little acetate of soda. According to Lowitz, a preferable method, as affording it still more concentrated and pure, is to mix three parts of the acetate of soda with eight parts of super-sulphate of potassa, both salts being perfectly dry and in fine powder,

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* Crell's Chemical Journal, vol. i. p. 242.

and to distil from this mixture, in a retort, with a gentle heat. By this process, seven pounds of concentrated acid, crystallizable by cold, may be obtained from 300 pounds of common vinegar *.

It was also long known, that from certain metallic salts formed from vinegar, a very strong acid could be procured by distillation. The salt usually employed for this purpose, is that formed by the action of vinegar on copper, the Verdigris of commerce. It is reduced to a fine powder, which is dried by a moderate heat. It is introduced into a retort connected with a receiver, and urged with a fire gradually raised: the portion that first comes over is weak, and is therefore to be removed; it is succeeded by an acid liquor extremely strong, and having a pungent suffocating odour. As obtained by the first distillation, it holds a small quantity of oxide of copper dissolved, from which, however, it may be freed by a second distillation, with a more gentle heat. The acid procured by this process, had formerly the name of Radical Vinegar.

It having been observed, that this acid differed in several of its properties, and still more in its saline combinations, from the acid which exists in distilled vinegar, even when this is concentrated by freezing, the opinion was maintained, that there is an essential difference between them. Berthollet, in particular, at an early period investigated this difference. Having concentrated distilled vinegar by freezing, and brought the acid obtained from verdigris by heat, to the same specific gravity by dilu-

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* Crell's Chemical Journal, vol. ii. p. 29.

tion, he observed, that the latter had a taste and odour more pungent than the former; it appeared to exert a stronger attraction to the alkalis, and to form with them combinations more intimate, and differing in their properties, from those formed by the other*. The difference between them, he supposed owing to the oxygen received by the acid from the oxide of copper, in its production from verdigris by heat; and according to the theory then maintained, to the transfer of phlogiston at the same time from the acid to the copper. The two acids thus came to be regarded as differing in their degree of oxygenizement, and were afterwards distinguished by the names of Acetous and Acetic Acids.

Adet some years ago called this opinion in question. From examining with attention the products of the decomposition of the acetate of copper by heat, he found reason to conclude, that the acid expelled from it receives none of the oxygen of the oxide, but is the same as that which existed in the salt, except that it contains less water. He compared this acid too, with that disengaged by sulphuric acid, without the application of any high heat, from acetate of copper, and acetate of potassa, and found them precisely the same. He found it impossible to oxygenize the acetous acid, so as to convert it into acetic. And in examining the actions of these acids on a number of substances, metallic, earthy, and alkaline, and the compounds they form, he found them perfectly identical, and equally so, allowing for the dilution, with distilled vinegar. He concluded, therefore, that the acetic acid expelled by heat from its metallic salts, does not receive oxygen: that it exists in one uniform degree of oxygenizement: that there is no acetous acid, therefore, different from the acetic; and that the apparent differences between the two acids so named, arise merely from the one being a little weaker or more dilute than the other *. Gren, it may be remarked, had held the same opinion.

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* Mémoires de l'Acad. des Sciences, 1783, p. 403.

Chaptal, in a memoir subsequent to Adet's, still maintained the opinion, that there is an essential difference between these two states of acetic acid; a difference which he sought to establish by experiments on their solvent power, their power of saturation, and their combinations: but he regarded this difference as depending, not on a different degree of oxygenizement, but on a different proportion of carbon in their base: the acetous acid existing in verdigris, losing, when it is expelled by heat, a portion of its carbon, which is attracted partly by a portion of the oxygen of the metallic oxide, and partly by the oxide itself, which passes nearly to the metallic state †. A similar opinion had been advanced by Perés: while Dabit revived and endeavoured to support by experiment the opinion, that these acids are in a different degree of oxygenizement ‡. Darracq has more lately, however, examined the subject, and has found the conclusions of Adet just. He repeated his experiments and found them correct; and added others, from which it resulted, that when the two acids are brought to the same

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* Annales de Chimie, tom. xxvii. p. 299.

† Nicholson's Journal, 4to, vol. ii. p. 518.

‡ Philosophical Magazine, vol. x. p. 334.

specific gravity, there is scarcely any difference between them in their physical properties, except that the smell of the acetic is a little empyreumatic. Their chemical properties were also alike, and their combinations the same. The acetous, submitted to the action of substances capable of affording to it oxygen, was not changed: nor by analysis did they afford different proportions of charcoal. Common vinegar, however, contains a quantity of mucilaginous or extractive matter, which Darracq found not to be altogether separated from it by distillation, and a portion of which even adheres to the acid in its saline combinations. The presence of this, and of a portion of water in what has been named Acetous Acid, somewhat disguise its properties; and by abstracting them by distilling this acid repeatedly from muriate of lime, an acid was obtained equally strong with the acetic, and having an odour as pungent and not empyreumatic. This may be regarded as the pure acetic acid.

There exists, therefore, as Darracq has remarked, only one acid of vinegar; which being at its maximum of oxygenizement, ought, in conformity to the principles of the modern nomenclature, to be named the Acetic. Its salts must be denominated Acetates; and the salts named Acetites, as distinct from these, have no existence *.

The acetic acid is extracted from the metallic salts in which it exists, by other methods than merely by the application of heat; in particular, by employing the affinity of some other concrete acid to disengage it, assisted by heat. It can thus be obtained from acetate of lead, by

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* Philosophical Magazine, vol. xiii. p. 12,

the intervention of sulphate of copper or of iron. A process of this kind, given by Badollier, is to expose to heat, in a retort, a mixture of equal parts of sulphate of copper and acetate of lead, as long as any acid comes over *. This has been introduced into the Pharmacopœia, substituting sulphate of iron for sulphate of copper. The acid thus procured, however, is much weaker, and, according to the observation of Debuc, confirmed by the experiments of Planche and Boullay, always contains sulphurous acid; which, however, according to the former chemist, may be abstracted by distilling it from black oxide of manganese, mixed with a very small quantity of carbonate of potassa †.

Acetic acid, in its highest state of concentration, such as that in which it is obtained when expelled from acetate of copper by heat, or when distilled repeatedly from muriate of lime, has a fragrant, and at the same time very penetrating smell, irritating the nostrils strongly: it is also so caustic as to inflame the skin: its acid taste is strong, even when it is largely diluted with water: it is colourless, and has a specific gravity of 1.0626. In its diluted state, as in that of distilled vinegar, its smell is much more faint, but is still agreeable, and its taste is merely sour.

This acid is capable of congelation, when it forms foliated arborescent crystals; and, according to the observations of Lowitz, it suffers this change, and presents very different results, according to its degree of concentration. If much diluted, as in common distilled vinegar, it is the

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* Annales de Chimie, tom. xxxvii. p. 111.

† Nicholson's Journal, vol. xiii. p. 42.

water that freezes, leaving a stronger acid uncongealed; if, on the contrary, the acid exposed to cold be more concentrated, it congeals, and the part that remains liquid is more watery. When strong, it congeals, according to his account, at the temperature of 32°, and remains solid even at a higher temperature *. With regard to this, however, there is some obscurity; for concentrated acetic acid does not freeze at a much lower temperature, and the acid distilled from charcoal, Lowitz himself remarks, requires a temperature lower than 20° of Fahrenheit.

This acid is very volatile: its odour is diffused through the atmosphere, when it is exposed to it, and becomes gradually weaker; and, by a moderate heat, it is converted into vapour: this vapour readily catches fire on the approach of an ignited body; and hence the acetic acid affords one of the best examples of an acid retaining the property of inflammability.

This acid combines with water in every proportion, and, when it is concentrated, the temperature rises from their combination.

Acetic acid combines with the alkaline and earthy bases. Its salts are denominated Acetates, or formerly, as they are generally prepared from distilled vinegar, which was considered as acetous acid, Acetites. They are very soluble in water, and the greater number of them have such an affinity for it as to be deliquescent, and not easily crystallized: the acetic acid is easily disengaged; and they are decomposed by heat, the greater part of the acid

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* Annales de Chimie, tom. x. p. 215.
Crell's Journal, vol. i. p. 245. 252.

suffering decomposition, and leaving a residuum of charcoal.

Acetate of Potassa is prepared by saturating the alkali of carbonate of potassa, by the addition of distilled vinegar. The liquor is evaporated to a dry mass: this is of a brownish colour, from the presence of a small quantity of extractive matter derived from the vinegar. If it be melted and kept in liquefaction for a short time, on dissolving it again in water, the extractive matter separates in flakes; the solution when strained is limpid, and when evaporated affords a salt perfectly white. It is soft, and of a very distinctly foliated texture, whence it received formerly the absurd name of Terra Foliata Tartari. Its concentrated solution affords, when exposed to cold, prismatic crystals. This salt is so deliquescent, that, even on a few minutes exposure to the atmosphere, its surface becomes humid: it does not require more than its weight of water for its solution at 60°: it is also soluble in alkohol. Its watery solution, like that of the other acetates, decomposes spontaneously; and when the dry salt is exposed to heat, its acid is decomposed, an empyreumatic oil and acid pass over, with a little ammonia, and much carbonic acid and carburetted hydrogen gases; a considerable quantity of charcoal remaining, mixed with carbonate of potassa.

Acetate of Soda, prepared by saturating carbonate of soda with distilled vinegar, is, by evaporation of its solution until a pellicle form on its surface, obtained when the fluid cools, crystallized in striated prisms. Its taste, like that of the preceding salt, is sharp and bitter: it is not deliquescent, but is easily soluble in water, requiring nearly three parts at 60°. It is decomposed in the same manner as the acetate of potassa.

Acetate of Ammonia, formed by saturating carbonate of ammonia with distilled vinegar, has been long known under the name of Spirit of Mindererus, having been employed in medicine as a diaphoretic. It is not easily obtained crystallized, as it is so volatile that its solution cannot be concentrated by evaporation: by a very slow evaporation, however, it may be obtained in acicular prisms; and it can be crystallized by sublimation. It is very deliquescent and soluble.

The combinations of this acid with the earths do not form compounds of much importance. Acetate of barytes crystallizes in acicular prisms, which are efflorescent, and, at the same time, very soluble in water. Its taste is bitter. As it is decomposed by the alkaline carbonates and sulphates, it is sometimes used as a test to discover carbonic and sulphuric acid. Acetate of strontites affords, by evaporation of its solution, slender crystals, which are soluble in water, requiring not much more than two parts for their solution, and which are not altered by exposure to the air. Acetate of lime is obtained by evaporation and cooling, in fine prismatic crystals of a silky lustre, efflorescent, soluble in water, and, as is observed by Mr Kirwan, still more soluble in alkohol. Its taste is bitter. Acetate of magnesia crystallizes, but with difficulty, its solution usually affording, on evaporation, a viscid deliquescent mass, abundantly soluble both in water and alkohol: its taste is sweetish. Acetate of argil, prepared by digesting the acid on the earth, forms small needle-like crystals, soft, and having an astringent taste. This salt is prepared for its application as a mordant, as has been already remarked, by decomposing acetate of lead by sulphate of argil. Acetate of glucine is easily formed by direct combination: the solution does not crystallize, but is reduced, as Vauquelin found, by evaporation, to a gummy-like substance, which remains long ductile, and dries slowly: its taste is sweet and astringent. Acetate of zircon is likewise gelatinous and uncrystallizable, and has an astringent taste. Acetate of ittria can be obtained by evaporation of its solution in crystals, which are thin plates, and of a purple colour.

Acetic acid, in its various states of concentration, acts more or less powerfully on the metals, and, in general, combines with facility with them when they are previously oxidized. Some of these combinations, particularly those with lead and copper, are extensively used.

Gold, silver, and platina, are not affected by it in their metallic state, but, when oxidized, are dissolved by it. The acetic solution of gold, it is remarked by Bergman, affords fulminating gold, when acted on by ammonia. The acetate of silver crystallizes in prisms, which are very soluble, and have a sharp metallic taste.

Acetate of quicksilver is different in its properties, according to the state of oxidizement of the metal. That in which the metal is imperfectly oxidized is best obtained by decomposing a solution of nitrate of quicksilver, in which the metal is in that state, by mixing it with a solution in tepid water of acetate of potassa: very delicate crystals, in the form of spangles, of a white colour and beautiful silvery lustre, form quickly, and are deposited as the solution cools. Its principles have so weak an affinity, that it is decomposed by water alone: if a large quantity be employed to wash it, it then becomes yellow: the whiteness is immediately restored, by washing with a little distilled vinegar: when dry, it forms a soft foliated mass: its taste is mild, but metallic. That which is formed by digesting the acid on mercury more highly oxidized, as on the red oxide, is more acrid and soluble.

Copper forms with this acid combinations of some importance, from their use in medicine and the arts. What has been named Verdigris is a sub-acetate of copper. It is prepared by stratifying copper plates with the husks of grapes, after the expression of their juice, and when they have been kept for some time imperfectly exposed to the air, in an apartment warm but not too dry, so as to pass to a state of fermentation, whence a quantity of vinegar is formed. The copper plates are placed in jars in strata, with the husks thus prepared, which are covered. At the end of twelve, fifteen, or twenty days, these are opened: the plates have an efflorescence on their surfaces of a green colour and silky lustre: they are repeatedly moistened with water; and at length a crust of verdigris is formed, which is scraped off by a knife, is put into bags, and dried by exposure of these to the air and sun. It is of a green colour, with a slight tint of blue *.

In this preparation, the copper is oxidized, probably by the atmospheric air, aided by the affinity of the acetic acid; and a portion of this acid remains in combination with the oxide, not sufficient, however, to produce its

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* Account of the Manufacture of Verdigris, by Chaptal, Philosoph. Magazine, vol. iv. p. 71.

saturation. When acted on by water, the acid, with such a portion of oxide as it can retain in solution, are dissolved, and the remaining oxide is left undissolved. From this analysis of it by the action of water, Proust inferred, that it consists of 43 of acetate of copper, 27 of black oxide of copper, and 30 of water, this water being not accidental, but existing in it in intimate combination *.

The proper acetate of copper is prepared by dissolving verdigris in distilled vinegar: the solution, when sufficiently evaporated, affords masses composed of prismatic crystals, aggregated, of a deep green colour when newly broken, but which become of a light green from efflorescence on exposure to the air. This salt is soluble in water, and also in alkohol: it has a strong metallic taste. It consists, according to Proust, of 39 of oxide and 61 of acid and water. Both it and verdigris are used as pigments, in some of the processes of dyeing, and in medicine on account of their escharotic power.

With lead, acetic acid forms combinations of some importance. Cerusse, or white lead, is formed by its action on the metal, plates of lead being exposed to the vapours arising from boiling vinegar, and the metal being oxidized by the action of the air, aided by the affinity of the acid. This has been regarded either as an oxide or a sub-carbonate of lead; though it appears probable, that it should contain some acetic acid. It serves as the basis from which the more perfect salt, the sugar of lead of commerce, is formed: the cerusse, in

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* Journal de Physique, tom. lxi. p. 114.

fine powder, is boiled in distilled vinegar, the vinegar being poured off as it loses its acidity, and fresh quantities being successively added. The liquors thus procured are then evaporated nearly to the consistence of honey; and, on cooling, masses are formed, consisting of a congeries of needle-like prisms. From the account given by Pontier of the manufacture of this salt, it appears, that it is also formed by exposing plates of lead to the action of distilled vinegar and of the atmospheric air: the plates, as they are incrusted with oxide at the surface of the vinegar, are plunged to the bottom, until this oxide is dissolved, and are again raised to the surface. The acid is thus at length saturated, and, by evaporation, the solution is brought to crystallize *.

This salt was regarded as the neutral acetate of lead. From the researches of Thenard, however, it appears, that it is a super-acetate, or contains an excess of acid, which modifies its properties. A manufacturer of sugar of lead having found, that in the method in which he conducted his process, the salt did not crystallize in the usual form, but in plates, Thenard examined this product, and found it to be the neutral acetate, while the common sugar of lead has an excess of acid. The latter, according to the analysis of it by this chemist, consists of oxide of lead 58, acetic acid 26, and water 16 †. The form of its crystals is a slender four or six sided prism bevelled at the extremities; its colour white, or frequently of a yellowish tinge, with a silky lustre; its taste is sweet and styptic; it is slight-

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* Annales de Chimie, tom. xxxvii. p. 268.

† Nicholson's Journal, vol. vi. p. 223.

ly efflorescent ; is easily soluble in water, requiring about 24 parts for its solution, but at the same time appears to be partially decomposed, as the solution, even with distilled water, is turbid ; a small quantity of a white powder is deposited, and the salt which remains dissolved, has probably a still greater excess of acid than the original salt. It is decomposed very readily by all these salts, which contain an acid that forms an insoluble compound with oxide of lead, and is hence sometimes used as a test to discover their presence. It is also decomposed by heat, and gives acetic acid diluted and empyreumatic.

The neutral acetate is described by Thenard as crystallizing in plates : it has a less perceptible saccharine taste than the super-acetate ; it effloresces slightly in the air ; is less soluble in water, and forms a solution which is precipitated abundantly by carbonic acid, while that of the super-acetate is precipitated sparingly. It dissolves in vinegar, and on evaporation gives needle-like crystals. It consists, according to his analysis, of oxide of lead 78, acetic acid 17, water 5.

Acetic acid dissolves iron, the metal being oxidized at the expence of the water. The solution is of a reddish brown colour ; has a sweetish astringent taste ; and by evaporation affords a gelatinous mass, which is deliquescent and easily decomposed by heat. The use of this solution as a mordant in calico-printing, has been already mentioned.

The remaining metallic acetates present few important results, and many of them have not been particularly examined. The acid dissolves tin only in small quantity [illegible] solution when evaporated is viscid, and has a fœtid smell. Zinc is dissolved by it very readily, and by evaporation crystals in thin plates are obtained, which burn when thrown on ignited fuel, with a blue flame, and are decomposed by heat. This salt is also formed by decomposing acetate of lead by sulphate of zinc. Nickel is dissolved by acetic acid, and the solution, by evaporation, gives crystals of a green colour. Oxide of cobalt is dissolved by it; the solution is of a pale rose colour, and forms a sympathetic ink. Antimony and bismuth are scarcely affected by it: the vitrified oxide of antimony, however, appears to be dissolved in small quantity. Oxide of arsenic is said not to combine directly with it; but when heated with acetate of potassa, a liquor is formed, fuming and having a very fœtid odour, and which the Dijon Academicians found inflamed spontaneously, on exposure to the air, and exhaled a dense fœtid vapour.

Acetic acid acts on several of the vegetable products. Mr Hatchet found, that it dissolves resins and gum-resins readily, without altering their properties. It also dissolves gluten, as has been already observed. It is a powerful solvent of camphor and essential oils; a property observed by Mr Henry, and applied to the preparation of what has been named Aromatic Spirit of Vinegar; a perfume more stimulating and more grateful, than the essences commonly formed from the volatile oils. It combines with alkohol, and when its action is promoted by heat, converts it into a species of ether, which has been already noticed.

The composition of acetic acid is not very well determined. As it affords the usual products of the vegetable acids when decomposed by heat, it is obvious that like them it contains carbon, hydrogen, and oxygen. Lavoisier, from the observation, that ammonia is given out in the decomposition of acetate of potassa by heat, supposed, that a portion of nitrogen might exist in the composition of the acid. Proust has found, that not only ammonia, but also prussic acid, is produced in the decomposition of acetic acid by heat; which he therefore considers as adding probability to the conclusion of Lavoisier *.

Acetic acid, in its various states of dilution and purity, is applied to numerous uses. Vinegar is one of the acids that has been longest known, and is extensively used as a condiment and an antiseptic. It is employed in medical practice, and in a number of the processes of pharmacy. And its saline and metallic combinations are used in several of the arts, as has been already stated.

SECT. III.

OF THE PUTREFACTIVE FERMENTATION.

PUTREFACTION is a process to which animal matter is more peculiarly liable. Some vegetable substances, however, likewise undergo it; and if others, in the ultimate spontaneous decomposition to which they are liable, do not give out those offensive products which characterize the putrefaction of animal matter, they so far present similar results, that their composition appears to be completely destroyed; their principles enter into new combin-

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* Journal de Physique, tom. lvi. p. 103.

ations, which escape in the aërial form; and they at length leave nothing but the small quantity of earthy and metallic matter, which the vegetable substance had contained. As this change follows the acetous, and has been supposed to be in general preceded by it, in a degree more or less marked, it has been considered as the last of the three stages of the process of fermentation, and has been distinguished by the epithet Putrefactive.

Every kind of vegetable matter is liable to this species of decomposition: there is none but what ultimately decays, though some resist it, or preserve their composition much longer than others. Those suffer it most quickly which are soluble in water; and any vegetable principle dissolved in this fluid, passes very speedily into it: the surface of the liquor appears covered with a mould; various elastic fluids are disengaged, and at length it is entirely decomposed. Those which are not perfectly soluble, if merely kept humid, present nearly the same results. Oils and resins, which refuse to unite with water or imbibe it, resist any change of this kind for a long period, and can indeed scarcely be said to be subject to it.

The same circumstances favour this species of spontaneous decomposition, which favour the others, particularly humidity, and a moderate heat. Any species of vegetable matter, kept perfectly dry, is long in exhibiting any sign of alteration or decay. A certain temperature, which must be less, however, than what will dissipate the humidity, hastens the decomposition, by favouring the approximation and consequent exertion of the affinities of the constituent elements. And the presence of the air often promotes it; at the same time, however, modifying the results.

The gases which are disengaged during this decomposition, are of course combinations of the principles of the vegetable substance. According to Saussure *junior*, they are compounds of hydrogen with carbon, forming inflammable gases and carbonic acid. The former appear principally when the action of the atmosphere is excluded, by the substance being immersed under water: the latter is produced when the air is admitted, and its production depends in a great measure on the action of the oxygen of the atmosphere *. A portion of water appears also to be formed, by the union of part of the oxygen and hydrogen of the vegetable matter.

The principal difference between this species of decomposition, and the putrefaction of animal matter, is, that there is no evolution of ammonia, or of those fœtid combinations which characterize the latter. This is owing to the absence of nitrogen, which is essential to the formation of these. And accordingly, those varieties of vegetable matter which contain this element, present, in their ultimate decomposition, results extremely similar to those of animal substances: such is particularly the case with all those which contain gluten, and with gluten itself in its pure form.

The residual matter of vegetable substances, after this species of decomposition, frequently contains a large proportion of carbon, especially when formed from those principles in which this element is abundant, as from the ligneous matter; and this may remain long unaltered, the other principles which could re-act upon it having been abstracted in the progress of the decomposition. A residuum of this kind forms that black soft matter which has been named Vegetable Mould, and which constitutes so important a part of the soil.

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* Recherches Chimiques, p. 157.

When this is obtained free from the undecomposed vegetable matter more or less mixed with it, it appears from the researches of Saussure, who has particularly examined it *, to be nearly uniform in its composition and properties. Subjected to distillation, it gave carburetted hydrogen, and carbonic acid gases; water holding in solution acetate and sometimes carbonate of ammonia, and a small quantity of empyreumatic oil, leaving charcoal, with various saline and earthy ingredients. From these products it follows, that the mould contained less oxygen, more carbon and more nitrogen, than the vegetable matter from which it had been formed; though part of this nitrogen must probably have been derived from the animal matter unavoidably mixed with it.

The acids do not exert any very striking action on this mould; they dissolve its earthy and metallic ingredients. The fixed alkalis dissolve it almost entirely, and evolve ammonia during the solution. Alkohol merely takes up a little resino-extractive matter. Water likewise dissolves a small quantity of extract.

Saussure has remarked, as has been above stated, that vegetable mould, though the result of the putrefactive process, is not itself susceptible of putrefaction, but even

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* Recherches Chimiques, p. 162.

rather retards it; hence it remains unaltered, evidently from the cause already assigned, that no other principles are present in sufficient proportion to act on the carbon accumulated in it. This, however, is to be understood of it, only when the air is excluded; for when exposed to the atmosphere, it suffers a gradual change, until it is entirely decomposed. The oxygen of the air combines with its carbon, forming carbonic acid, as Saussure found by inclosing it over quicksilver, in atmospheric air or oxygen gas. While this proceeds, the abstraction of carbon appears to allow part of the oxygen and hydrogen of the mould to combine and form water; for it loses more of its weight than can be accounted for, merely from the quantity of carbon abstracted. These changes continue to proceed in a certain relation to each other, and terminate at length in the entire decomposition, leaving the earthy and metallic substances originally contained in the vegetable matter. We perceive from this view, how necessary the frequent turning up of the soil is, to enable the vegetable mould to form a proper manure, by decomposing, and affording carbonic acid to the growing plant. And we discover also the cause of the inertness and unfertility of that accumulation of it, which principally constitutes peat and morass, and which, if not subjected to certain operations, remains for ages unchanged.

SECT. IV.

OF THE SPONTANEOUS DECOMPOSITION OF VEGETABLE MATTER, LEAVING CARBON PREDOMINANT.

WHEN the slow and spontaneous decomposition of vegetable substances is conducted under peculiar circumstances, the result is the accumulation of carbon in the residual matter; and beyond this the decomposition frequently does not proceed. The circumstances on which this is dependent, are not, perhaps, perfectly determined; but they seem to be, principally, a due humidity, a certain degree of compression, and the exclusion of atmospheric air. These circumstances are all present when the substance is buried to some depth in the earth, and it is in this situation that this species of spontaneous decomposition is best exemplified.

We can perceive, so far at least, how these circumstances operate in giving rise to this peculiar result. A certain degree of humidity is requisite to favour the mutual actions of the principles of the vegetable matter. Were the atmosphere freely admitted, its oxygen would modify these actions, and, in particular, by its affinity to carbon, would abstract the greater part, and allow the remaining principles to enter into other combinations. Compression seems to operate by preventing, or at least opposing the formation of elastic compounds: were it not present, it is probable, that, in the re-action of the elements of the vegetable matter, the oxygen would combine part.

ly with hydrogen, and form water, and partly with carbon, and form carbonic acid. But compression opposing an obstacle to the formation of the latter substance, the combination of oxygen with hydrogen is more effectually determined, and thus carbon remains predominant in the residual matter.

It is obvious, also, that those kinds of vegetable matter which contain the largest proportion of carbon will be those most susceptible of this species of decomposition, and which will exhibit most completely this result. Hence we find it conspicuous in wood.

On these principles, I conceive, may be explained this species of decomposition, the existence of which cannot be doubted, since we perceive it particularly exemplified in the instance just now quoted, of wood that has been kept humid, and buried to a certain depth. And the various coally and bituminous substances which are found in the earth have been probably formed by some such process. Their origin from vegetables is clearly marked in their composition and properties: they are inflammable; afford, by destructive distillation or combustion, the usual products of vegetable matter; the remains of vegetable and animal substances are often found intermixed with them, indicating their origin; and we can even trace the gradation from wood slightly changed to those which are most remote from the ligneous texture. These I propose, therefore, to consider under this section, as concluding the history of vegetable substances.

Bitumens are of various degrees of consistence, liquid, soft, or solid, and consist of carbonaceous matter, more or less pure. Considering their arrangement chemically, they may be comprehended, perhaps, under the four following species,—Coal, Petroleum, Amber, and Mellite; the two first including a number of varieties.

Coal consists essentially of carbonaceous matter and bitumen, united with more or less earthy matter; and these varying considerably in their proportions, numerous varieties of it are formed. Those which contain much bitumen are highly inflammable, take fire readily, and burn with a bright flame: those in which the proportion of bitumen is less, and in which the carbon predominates, burn less vividly; they require a higher heat to kindle them, and burn without flame, or only with a red glow. During the combustion, the products are principally water and carbonic acid gas; sulphurous acid is also formed in small quantity, derived, probably, principally from the sulphuret of iron contained in the coal; and a portion of ammonia, the origin of which is not very obvious, appears also to be formed, as sulphate of ammonia is always contained in the soot collected from the combustion of coal. The earthy matter contained in coal remains after the combustion, and, except in some varieties, is not in large proportion.

The bituminous part of coal is separated from the carbonaceous part by the application of heat. We perceive this separation in its combustion in a common fire; the coal, when first kindled, swelling and softening, exhaling a kind of bitumen, and burning with much smoke and light; while, after a certain period, these appearances cease, and the coal burns only with a red light. The separation is effected more completely by the application of heat in close vessels: the bitumen is melted out; there is disengaged at the same time a large quantity of ammonia, partly in the state of carbonate, with a quantity of empyreumatic oil, and a gas, approaching in its nature to olefiant gas, which burns with a bright flame, and has been applied, as already stated, to the purpose of procuring artificial light. When this species of distillation is continued until these products are no longer formed, the carbonaceous matter of the coal remains in the state of coak, which, if the air be admitted and the temperature sufficiently high, burns nearly as charcoal, and without flame.

This decomposition of coal by heat has been carried on on a large scale, with a view to collect the products; the bituminous matter, or mineral tar, as it is named, being applied to the uses to which vegetable tar and pitch are employed, and the coaked coal being used with advantage in the smelting of metallic ores, and for other purposes. The process was established in this country by Lord Dundonald, and has also been carried on with advantage in other countries.

The general chemical history of coal is almost entirely confined to these facts, as the action of other substances upon it has been little attended to, and does not appear indeed to be very energetic. Mr Hatchet has found, as has already been stated, that, when treated with nitric acid, it affords artificial tannin; and those varieties of it which contain bitumen, yield, at the same time, by this treatment, a matter intermediate in its characters between extract and resin, and which, by the farther action of nitric acid, is converted into tannin *.

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* Philosophical Transactions, 1806.

Numerous varieties of coal exist, deriving their distinctions as objects of mineralogical description partly from their state of aggregation, but principally from the proportions of their bitumen and carbon. As subjects of chemical history, these latter distinctions are of course those which are chiefly to be attended to. The series may be briefly described, according as they are connected, on the one hand, with vegetable matter, and, on the other, with carbon, evidently not of vegetable origin.

In this order, what has been named Bituminous Wood, from the ligneous texture remaining, must find the first place. This texture is very distinctly marked, and even the external shape of the branches and stems of trees, and the annual rings of the wood, are distinctly preserved, so as to resemble wood imperfectly charred. Its colour is brown, of different shades: it is opaque, with little lustre, has little density or hardness, and is so light as nearly to float on water. It burns with a clear flame, and with a bituminous odour, somewhat similar to that from wood; and it leaves a small quantity of white ashes, similar to those from wood. It is found in beds, generally in alluvial land, and in masses with other varieties of coal, or imbedded in rocks of the trap formation. The Bovey Coal, near Exeter, is an example of it, as is also the Surturbrand of Iceland.

Connected with this species, are what have been named Earthy Bituminous Wood, or Earthy Coal, which is found of a loose consistence, nearly earthy, dull, of a blackish brown colour, light and soft; which occurs along with the bituminated wood, and passes into it; and Brown Coal, as it has been named from its colour, which occurs massive, having an imperfect conchoidal fracture, sometimes fibrous and woody, soft and light, which burns with a blue flame, and gives a smell like bituminous wood, and which, like the other varieties, occurs in alluvial land. Mr Hatchet found a coal of this description to afford by distillation, besides a portion of water slightly acidulous, amounting to 30 parts from 100, bitumen in the proportion of only 10.5, charcoal 45, and carbonic acid and carburetted hydrogen gases 14.5. The earthy varieties are some of them used as paints; umber is one of them: and some of them which contain much earth and sulphuret of iron are wrought for the manufacture of alum.

What has been named by Werner, Black coal, the species which is by far the most abundant, is subdivided into several varieties from slight differences in properties. That named Pitch coal, from its resinous lustre and smooth conchoidal fracture, forms the variety which has been known under the name of Jet, and which, from the closeness of its texture, is capable of being fabricated into ornaments. Its colour is deep black, and the ligneous texture is often to be perceived in it. It burns with flame, and a bituminous smell not unpleasant. Cannel coal, so named from affording much light in its combustion, has, like the preceding, a smooth conchoidal fracture, a resinous lustre, and a black colour, and is sometimes applied to similar uses, though used also abundantly as fuel. It burns without melting; its light is at first bright, but soon ceases, and it then leaves a large coally residuum. It contains, according to Mr Kirwan's analysis, 75.2 of carbon, 21.68 of bitumen, and 3.1 of foreign matter. The Slaty coal forms the variety most abundant in this country: its principal fracture is slaty, the crose fracture small grained uneven; its colour is black, frequently with a shade of grey, and sometimes iridescent; its lustre resinous; it is soft, and has a specific gravity of about 1.25. It softens, cakes, and burns brightly, and leaves, when entirely burnt, a small residuum of ashes. It appears, therefore, to contain more bitumen than the preceding varieties; the proportion in different kinds appears from Mr Kirwan's analysis to vary from 24 to 40, with from 53 to 70 of carbon, and 2 or 3 of earthy matter. The Foliated coal, as it has been called, approaches to the slaty, being distinguished by its fracture and its greater lustre: it is also softer, and appears to contain more bitumen. Columnar coal is so named from occurring in columnar distinct concretions, and is more rare. It burns without flame or smell, and hence is probably connected with the next species.

Blind coal, the Anthracite of mineralogists, the Glance coal of Werner, consists almost entirely of carbonaceous matter. It burns therefore without flame, without exhaling any bituminous odour, and without softening or caking; nor does it continue to burn of itself until it is fully ignited, and then burns slowly. Kirwan found, that in deflagrating it with nitre, it required a larger quantity for its consumption than the other varieties of coal do, and even more than charcoal; and from this fact, as well as from its properties, Guyton, as has already been remarked, (vol. ii. p. 294), regarded its carbonaceous matter as in an imperfect state of oxidation, or approaching even nearer than charcoal does to carbon in its pure form. It constitutes the transition from coal to plumbago, nor only in its chemical relations, but in its external properties. Its colour is usually black, sometimes inclining to steel grey; its lustre is shining, and nearly metallic; its fracture is slaty; its hardness such as to yield easily to the knife; it is brittle, and has a specific gravity of about 1.5. It occurs generally in primitive rocks, or in those of transition in imbedded masses, in beds and veins. It has also been discovered by Mr Jameson in the independent coal formation in the island of Arran, and is not therefore exclusively of early formation as had been supposed. There appears no reason to infer that it is of vegetable origin. Brochant gives the following analyses of it, executed by Panzenberg and Dolomieu: that of the latter, there is reason to suspect, however, refers rather to a variety of graphite.

	Panzenberg.	Dolomieu.
Pure carbon	90	72.05
Silex	from 4 to 2	13.19
Argil	— 4 to 5	3.29
Oxide of iron	— 2 to 3	3.47
Loss	——	8.00

The following table gives the results of an analysis of different coals by Mr Kirwan, made by projecting a certain quantity of each on ignited nitre, observing how much nitre was decomposed or alkalized; and inferring from this what proportions of bitumen and carbon they contained, the carbon only being supposed to exert this operation. This assumption is perhaps not just, and several sources of fallacy attended the experiment. The last five coals in the table appear to be varieties of black slaty coal.

100 parts	Carbon.	Bitumen.	Ashes.
Maltha	8	—	—
Asphalt	31	68	—
Kilkenny coal	97.3	—	3.7
Compact cannel —	75.2	21.68	3.1
Slaty cannel — —	47.62	32.52	20
Whitehaven —	57	41.3	1.7
Wigan —	61.73	36.7	1.57
Swansey —	73.53	23.14	3.33
Leitrim —	71.43	23.87	5.20
Newcastle —	58	40	—

Coal is found in strata, which are of very various thickness, and which alternate, or are connected with various rocks of secondary formation, particularly with clay, slate clay, argillaceous ironstone, sandstone, limestone, grunstein, and basalt. They are also of limited extent, generally forming as it were patches or hollows filled up with the coal and its accompanying rocks, indicating partial formations.. Three formations of it have been supposed by Werner. The principal is what is named the Independent coal formation, from coal being the principal fossil belonging to it, and from its being found in insulated fields or patches, lying over other secondary rocks, or sometimes rocks of transition, and accompanied with the rocks above enumerated, the whole being distinctly stratified, generally horizontal, or not much inclined, and containing abundant impressions of organic remains. Besides this, coal is found, according to the same authority, in a formation subordinate to what is named the newest floetz formation, in which it is accompanied with wacken, basalt, greenstone, and argillaceous ironstone; and, lastly, some varieties of it, especially the brown coal, are found, as has been already remarked, in alluvial land.

Coal, excluding the anthracite or blind coal, is evidently of vegetable origin. We trace in it, as has been already remarked, the gradation from bituminated wood; we often discover in its varieties the ligneous structure, and even the remains of plants; and its chemical composition agrees with that of vegetable matter.

It is difficult, however, to determine in what manner it has been formed, or by what operations the vegetable matter from which it is originated has been so far modified as to have assumed the properties under which it exists. The discussion of this subject is indeed intimately connected with geological speculation; for the opinion which is adopted, must be connected with the general theory which is held with regard to the structure of the globe. In the geological systems of the present day, very different opinions are accordingly maintained with regard to the origin of coal: in the system of Werner, it is regarded as originating from vegetable matter, altered by operations conducted in the humid way: in the system of Hutton, it is supposed to have been formed by the action of subterranean heat, operating under partial compression.

Were the latter system received, and the theorist allowed the convenient assumption, that wherever coal had been formed, a *partial* compression had existed, the experiments of Sir James Hall have rendered it probable, that from such a cause a substance might be produced somewhat analogous to coal; as by a very moderate heat, applied under such compression both to vegetable and animal substances, as saw-dust and horn, he formed matter more or less bituminous *.

On the supposition that it is of aqueous formation, the process from which it may have originated may be conceived to be somewhat similar to that described in the beginning of this section, in which vegetable matter in a state of humidity, and under compression, has suffered decomposition from the re-action of its elements, these circumstances determining the combination of its oxygen principally with its hydrogen, so as to leave the carbon predominant. It may be supposed, " that vegetable matter carried to the sea, has, by the direction of currents, been deposited in banks, and that during this submersion it has suffered that slow kind of decomposition by which the greater part of its principles have been evolved in new combinations, while its carbon, with a portion of hydrogen, have remained; and this, mixed with more or less earthy matter deposited at the same time from the ocean, has in its soft state been consolidated by the force of aggregation, and has formed coal. The decomposition by which this has been effected, is probably analogous to that which we know animal matter, when immersed in water, suffers. Its hydrogen, azot, and oxygen, enter into various combinations, forming gases which escape; and its carbon retaining, by a chemical attraction, a portion of hydrogen in combination, remains, forming a species of fat. Carbon is still more abundant in vegetable than it is in animal matter; and this constitutes the principal dif-

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* Transactions of the Royal Society of Edinburgh, 1805.

ference between them. Vegetable matter, however, is liable to similar decompositions; and under the circumstances pointed out, it is reasonable to believe that changes of a similar kind, modified as to the result by the difference in the proportions of its principles, will take place: in other words, its residue will be more carbonaceous, but still with a proportion of hydrogen, so as to render it more or less bituminous. We accordingly find, that wood, by immersion in water, becomes first brown, and then black; and the ligneous fibre, by slow decomposition, is completely converted into a black mould, in which carbon predominates. It is easily conceivable, that this process being carried on under different circumstances, may proceed with various degrees of rapidity, and to a greater or less extent. Hence will originate different varieties of coal, some being much more carbonaceous than others; while their composition is also varied by the different quantities of earth deposited during their formation *."

Mr Hatchet has remarked, that observations on the state of wood, in submarine forests, demonstrate, that whether vegetables are totally or partially buried under the waves, or under the earth, they are not merely by such means converted even into the most imperfect sort of coal, and that therefore some process independent of these circumstances mnst have taken place in the formation of this substance. And having found, that from the action of acids on vegetable matter, products might be obtained more or less similar to bitumens, he has supposed, that

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* Comparative View of the Huttonian and Neptunian Systems of Geology, p. 208.

some such action, exerted by muriatic, or more probably sulphuric acid, may have contributed to the formation of coal *. It is not easy, however, to conceive how these could operate on collections of vegetable matter on the large scale, that must be supposed to account for the formation of strata of coal; and the consideration that wood is found long submersed without having been bituminated, perhaps only proves that the process is extremely slow, not that the change which it actually does suffer might not ultimately pass to that state.

THE substances which have been distinguished by mineralogists under the names of Asphaltum, Petroleum, and Naphtha, appear to be mere varieties of one species, and form a series which passes even into coal. Asphaltum forms the connection with pitch coal. It is of a black colour, and resinous lustre, without transparency: its fracture is conchoidal: it feels somewhat greasy; is light, and has a bituminous smell, when rubbed or heated. It melts easily, takes fire, and burns without leaving any ashes. It is found in veins, and in small masses, and also sometimes on the surface of lakes. Mineral pitch, or Maltha, is softer, has a degree of tenacity, and a strong bituminous smell. It is sometimes elastic, forming what has been named the Elastic Bitumen. A variety of this found in a vein of a lead mine near Castleton was examined by Mr Hatchet, who found it had all the properties of these bitumens, and who supposed, that it owed its elasticity to minute portions of air interspersed in its sub-

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* Philosophical Transactions, 1806.

stance; as, when melted, it completely lost the elastic property, and, at the same time, gave out a quantity of aërial fluid. This might, however, be only an accidental coincidence; and Mr Hatchet having since found, that there is a strict resemblance between the elastic bitumen and caoutchouc, in the changes they suffer from acids [*], it is not improbable that the property may depend on some peculiarity of combination. Mineral tar is more of a liquid consistence: it is tenacious, and of a reddish or blackish brown colour. Petroleum is semi-liquid, semi-transparent, of a reddish brown colour, and fœtid odour. Naphtha is of a lighter colour, more or less transparent, perfectly thin and liquid, light, so as to float on water, odoriferous, volatile, and inflammable. Through all these substances there is a perfect gradation; naphtha, by inspissation, becoming petroleum, and this, by the same operation, passing into asphaltum; and even the different specimens of these are frequently found in the same situation. These changes, as Mr Hatchet in his paper on bitumens remarks [†], appear to be caused by the gradual dissipation of part of the hydrogen of the bitumen, and the consequent developement of a portion of carbon. They also agree in their chemical characters, are inflammable, insoluble in water and in alkohol, but combine with fixed and essential oils, and are partially soluble in ether. They are not dissolved by the alkalis; are decomposed by the more powerful acids, especially by the nitric, which, as Mr Hatchet found, causes the production of a substance intermediate in its properties between extract and resin, and which, by the farther action of the acid, is converted into tannin.

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[*] Philosophical Transactions, 1806.

[†] Nicholson's Journal, 4to, vol. ii. p. 201.

There is some obscurity with regard to the natural sources of these bitumens. Those that are liquid are found generally exuding from crevices in the rocks which accompany coal, and frequently flow on the surface of water which has probably run over coal strata.

AMBER is usually placed among the bitumens, though it differs from them considerably in its properties. It is of a yellow colour, pale or deep, is often perfectly transparent, and has a shining lustre; at other times it is more or less opaque: its internal lustre is highly shining: it is inodorous, unless when heated, and is insipid: its fracture is conchoidal: it is brittle, and has a specific gravity of about 1.08. When rubbed it becomes strongly electrical: it was even in this substance that this property was first observed; and it is from the name under which it was known to the ancients, *Electrum*, that the term Electricity has been derived.

Amber occurs in fragments, or sometimes in large masses: it is found in layers of bituminated wood, often also buried in sand on the sea-shore. No very satisfactory theory has been given of its origin or formation. It often contains very perfect organic remains, especially insects, and sometimes leaves of vegetables,—a proof of its having been once perfectly fluid. It is found in greatest quantity on the shores of the Baltic, but occurs also in other countries.

With regard to chemical properties, amber approaches to the resins, but presents also some peculiarities, especially in affording an acid *sui generis*, when decomposed by heat.

When it is exposed to heat in close vessels, it softens and swells; a quantity of an acidulous liquor passes over; this is succeeded by a concrete acid, which condenses in flakes or needles; a considerable quantity of an oil highly empyreumatic, and of a deep brown colour, distils over; a black resinous-like substance forms the residuum.

When amber is heated in contact with the air, it inflames, burns with much smoke, and with a strong bituminous smell, and leaves little residue.

Water exerts no action on amber. Alkohol acts on it weakly, acquires colour and some tenacity from a portion being dissolved.

Hoffman observed, that amber reduced to powder, and boiled in a solution of pure potassa, is almost entirely dissolved. It combines with the alkali, and forms a kind of soap, and, in this respect, has therefore a near resemblance to the resins.

Amber is decomposed by the more powerful acids, which change it into a species of resin. Mr Hatchet found it yields abundance of artificial tannin, when subjected to the action of sulphuric acid, in the same manner as the resins and balsams.

There is one property in which it differs from the resins, that of not being dissolved either by the expressed or essential oils; but it becomes soluble by being roasted gently. Solutions of this kind are used as varnishes. This varnish is preferable to almost any other for a number of purposes. It dries speedily: it does not crack, and is extremely durable. In mixing with colours, it is also said to render them more brilliant, and preserve them better than the drying oils do. There is some difficulty, however, in preparing it, principally with regard to the heat to be applied. Ample directions have been given, in a dissertation on this subject by Nils Nyström *.

The empyreumatic oil obtained from the decomposition of amber by heat is thick, and of a dark colour: by distilling it repeatedly, with the addition of a little water, it becomes thinner and of a lighter colour, leaving at each distillation a little coally matter; and at length it may be obtained nearly colourless. It still retains a very fœtid smell: it is volatile and inflammable; is insoluble in water, and imperfectly soluble in alkohol. It also combines imperfectly with the alkalis. Liquid ammonia impregnated with it forms Eau de Luce. Concentrated sulphuric acid poured upon it produces considerable heat, and converts it into a yellow resin, having a fragrant odour, somewhat similar to that of musk.

The acid obtained by the same decomposition, the Succinic Acid, as it is named, is possessed of properties which sufficiently distinguish it. As first procured, a portion of empyreumatic oil adheres to it, and gives it colour and smell. From this it is not perfectly freed, even by repeated solution and crystallization. If charcoal powder recently prepared be added to its solution in water, and the solution be made to filtrate through the charcoal, it is obtained more pure, as it is also, according to Guyton, by

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* Philosophical Magazine, vol. vii. p. 233.

distilling a little nitric acid from it: or, according to a process given by Richter, it may be combined with potassa; the salt thus formed may be decomposed by acetate of lead; and the succinate of lead may, lastly, be decomposed by sulphuric acid.

This acid crystallizes in four-sided rhomboidal plates, which, when pure, are white; their taste is sour, and they redden infusion of litmus; they are rather sparingly soluble in cold water, requiring twenty-four parts for their solution, but are abundantly soluble in hot water; they are also soluble in alkohol. This acid is also volatile and inflammable. In these properties it bears some resemblance to benzoic acid. Like the other vegetable acids it has a compound base of carbon and hydrogen, as is proved by the usual products which it affords when it is decomposed by heat.

Succinic acid combines with the alkalis, earths, and metallic oxides, but few of these combinations present any important results. They have been examined by Bergman. Succinate of potassa crystallizes in triedral prisms, which are easily soluble in water; its taste is bitter: exposed to heat it decrepitates, and is decomposed. Succinate of soda crystallizes in nearly the same form; its taste is bitter, and it is also decomposed by heat. Succinate of ammonia appears under the form of needle-shaped crystals, having a saline and bitter taste, and volatile, so as to be capable of being sublimed. Succinate of barytes is of very sparing solubility in water. Succinate of lime affords long spear-shaped crystals permanent in the air, and not easily dissolved even by boiling water. Succinate of magnesia does not crystallize, but by evaporation forms a viscid mass. Succinate of argil crystallizes, according to Wenzel, in prisms.

The metallic succinates have been less examined. In general they are soluble and crystallizable. Succinate of iron, however, is insoluble, and from this property succinic acid has been employed as a test of this metal, and as a re-agent by which substances may be freed from it, succinate of potassa being added to any solution containing iron, and the succinate of iron being precipitated.

The oil and acid of amber have been employed in medicine, and have a place in the pharmacopœias, but they are nearly discarded from practice. Amber itself, when transparent, of a rich colour, and free from flaws, is cut and fashioned into various kinds of ornaments.

Mellite or Honey-stone has been placed among the bitumens, with which, though it differs from them considerably, it has some relations. In its external appearance it has some resemblance to amber: it is of a honey yellow colour, whence its name; is more or less transparent, and has the property of double refraction; its lustre is intermediate between vitreous and resinous; its surface smooth, its fracture conchoidal; it is brittle, and softer than amber; has a specific gravity of 1.6. It occurs generally crystallized; its crystals being octaedrons, dodecaedrons, or four-sided prisms acuminated by four planes. It becomes, according to Hauy, weakly electrical from friction. When heated in contact with the air, it becomes white, and, as Vauquelin remarked, burns without becoming sensibly charred, and leaves a white matter, which produces a slight effervescence with acids.

This substance is found in the layers of bituminated wood in Thuringia, and, as has also been affirmed, with mineral pitch in Switzerland. Its nature was unknown until it was analysed by Klaproth, who found it to consist of a peculiar acid, which has hence received the name of Mellitic Acid, united with argil*,—a discovery confirmed by Vauquelin, who found it likewise to contain small portions of silex and lime †.

The acid may be extracted from this substance, merely by the action of water, the water being boiled on the honey-stone; the acid is dissolved, the argil precipitates, and by evaporation the former can be obtained in a mass, which when subjected to the action of alkohol, so as to separate a portion of earthy matter, may be crystallized. Vauquelin procured it in his analysis, by adding the crystals of mellite in powder to a solution of carbonate of potassa: the mellitic acid combined with the alkali, disengaging the carbonic acid with effervescence; and on adding to the filtered liquor a little nitric acid to saturate the alkaline base, the mellitic acid was deposited in a few hours, crystallized in short prisms.

The acid thus crystallized has a yellowish tinge, and a slight acid taste, accompanied with bitterness. The colour and the bitterness may arise from a little bitumen attached to it. Exposed to heat it swells up, emits a dense smoke, is charred, and leaves a light coal: exposed to the flame of the blow-pipe, it gives at first a few scintillations like those of nitre, and is then quickly decomposed. It is sparingly soluble in water.

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* Analytical Essays, vol. ii. p. 89.

† Nicholson's Journal, 4to, vol. iv. p. 515.

Mellitic acid combines with the different salifiable bases, but these combinations have been only imperfectly examined by the two chemists by whom the honey-stone was analyzed. Mellate of potassa crystallizes in prisms: the crystals obtained by Vauquelin, by the process above described, appear to have been rather super-mellate of potassa, than the pure acid; as when decomposed by heat, the coal was highly alkaline. Mellate of soda crystallizes in cubes, and also in plates. The acid neutralized by ammonia, gives transparent six-sided prisms, which become opaque from exposure to the air. Added to the watery solution of barytes, strontites, or lime, it produces immediately a precipitate of a white powder, indicating the formation of an insoluble salt. If added, however, to muriate of barytes, it gives a precipitate in needle-like crystals; and with a solution of sulphate of lime, a granulated and crystallized precipitate. With the solution of silver it gives a white silky precipitate; with the nitric solution of lead, a white pulverulent very heavy precipitate; with that of mercury, a white precipitate, which ammonia turns black: and with that of iron a yellow precipitate.

Vauquelin has observed, that this acid is in many of its properties very similar to the oxalic, and he appears even disposed to conclude in favour of their identity. The only differences he found between them were, that the precipitate which mellitic acid causes in the solution of sulphate of lime, is less speedily manifested, and is crystalline instead of being pulverulent, like that formed by the super-oxalate of potassa; that it appears less acid to the taste than this acidulous salt; and that it swells up rather more by heat than it does;—differences very trivial, and which may arise from slight causes. One difference, however, between the two acids, more important, afterwards noticed by Vauquelin, is, that super-mellate of potassa, added to a solution of pure sulphate of argil, gave an abundant flocculent precipitate, while super-oxalate of potassa caused no precipitation.

Mellitic acid appears to be of similar composition with the vegetable acids; affording, when decomposed by heat, carbonic acid, carburetted hydrogen, an oil somewhat aromatic, a water slightly acidulous, and charcoal as a residuum. Vauquelin has observed, that it appears, like the oxalic acid, to contain a large proportion of oxygen, as in its decomposition it affords much carbonic acid, and only a small proportion of charcoal. Klaproth did not succeed in attempting to convert it into oxalic acid, by the action of nitric acid.

BOOK IX.

OF ANIMAL SUBSTANCES.

THE chemical history of Animal, like that of Vegetable Substances, may be comprised under three divisions. In the first may be considered, what relates to their formation, so far as this is dependent on chemical action. Under the second may be described, the varieties of animal matter; their chemical properties and combinations: And their history may be concluded, with an account of the decompositions they suffer, and the spontaneous changes to which they are liable.

CHAP. I.

OF THE FORMATION OF ANIMAL SUBSTANCES.

ANIMAL, like vegetable substances, are formed of a few simple principles; the differences in their properties arising from variations in the proportions, and in the modes in which these are combined. They are equally susceptible of decomposition, or even more so; the balance of affinities whence they exist, being altered by very slight causes, and their principles easily entering into new combinations.

There are certain chemical characters, by which the animal are distinguished from the vegetable products. They are, in particular, more liable to that species of spontaneous decomposition named Putrefaction. Vegetables in a humid state, pass into the vinous or acetous fermentation, or suffer that species of decomposition whence carbonic acid and carburetted hydrogen gases are disengaged, and charcoal remains. Animal substances are liable to none of these changes, or at least are little disposed to pass into them; they rather undergo the putrefactive fermentation, or their elements enter into new combinations, the principal of which are ammonia, and certain elastic fluids more compound than those formed in the decomposition of vegetable matter.

When vegetables are decomposed by heat, the products of the decomposition are empyreumatic oil and acid, carburetted hydrogen, carbonic oxide, and carbonic acid gases, the residuum being charcoal. Some likewise afford ammonia, but it is yielded only in small quantity, and by a few of them. Animal substances, along with the usual products of the analysis of vegetable matter, invariably afford a large quantity of ammonia when they are decomposed by heat. They give also some other peculiar products, particularly compounds of sulphur and phosphorus with hydrogen, the prussic acid, and phosphoric salts.

These differences between the animal and vegetable products, arise from the difference in their chemical composition. That of animal substances is more complicated than that of vegetable matter, as, besides carbon, hydrogen, and oxygen, they always contain nitrogen, and generally phosphorus and sulphur. The presence of these principles dividing the attractions subsisting between the carbon, hydrogen, and oxygen, weakens their force, and hence these complicated compounds are more liable to decomposition, and their elements have a powerful tendency to enter into binary or ternary combinations. To this cause is owing the great susceptibility of decomposition which characterizes the animal products.

The peculiar products they afford by their analysis, derive their origin from those elements which are peculiar to them, or which are at least contained in less quantity and less generally in vegetable substances. The nitrogen, in particular, which may be considered as the principle that peculiarly gives them their character, by combining with hydrogen, furnishes the ammonia, which is formed both during their putrefaction and their decomposition by heat: it forms a principal component part of the prussic acid, and it enters into the composition of the gases they give out. This predominance of nitrogen in animal matter, is clearly shewn by the action of the nitric acid, which disengages it in considerable quantity, and, if the experiment be properly conducted, without the acid itself suffering any decomposition.

Phosphorus is another substance present in the greater number of the animal substances, and almost peculiar to them. During their decomposition it enters into new combinations, particularly with hydrogen and nitrogen, and forms those compound gases, the extrication of which accompanies the putrefaction and decomposition by heat of those substances. If they are decomposed by the action of nitric acid, it is converted into phosphoric acid, and remains mixed, as Berthollet, in his observations on animal matter, shewed *, with the oxalic acid usually formed in that process. On its presence also depends the abundance of neutral salts, formed by the union of the phosphoric acid with the oxide of iron, the earths, and alkalis, which are so generally afforded by their analysis.

Sulphur is likewise a component part of several animal substances, and must of course enter into the composition of the products of their decomposition.

It may be added as another general difference in composition between animal and vegetable substances, that the former contain less carbon, and more hydrogen than the latter. Carbon appears to be the base of vegetable

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* Mémoires de l'Acad. des Sciences, 1785, p. 348.

matter, to which oxygen and hydrogen are attached. Hydrogen is perhaps the principal component part of animal matter combined with nitrogen, oxygen, carbon and phosphorus. Hence in the decomposition of animal substances, much empyreumatic oil is obtained, of which hydrogen is the chief constituent, while another portion of hydrogen is spent in the formation of ammonia. The predominance of hydrogen in their composition is shewn by another fact, observed many years ago by Berthollet as characteristic of animal matter, that when acted on by nitric acid, along with the oxalic acid which is always formed, there is also a formation of a species of oily or fatty matter, derived no doubt from a combination principally of hydrogen with carbon *. In general, the animal substances contain less oxygen than the vegetable, as they afford much less acid by their decomposition.

In investigating the formation of the animal products, there can be no doubt of the truth of the general proposition, that they are derived from changes effected by the animal system, on vegetable matter. All animals live directly or indirectly on vegetables, and derive from them their principal, almost their sole support. Before proceeding, therefore, to the particular consideration of the animal products, it is necessary to take a general view of the process by which they are formed. This leads to the consideration of Digestion, Respiration, and Secretion, the three functions which compose, by their union, the process of animalization. Though these

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* Mémoires de l'Acad. des Sciences, 1780, p. 120.

functions are in some measure regulated by laws peculiar to the living system, these undoubtedly do not suspend the exertion of the usual laws to which the matter concerned in them is subject. Affinities are exerted between the particles of that matter, and new combinations are established; and it belongs to chemistry, therefore, to trace these combinations and the circumstances by which they are modified, and thus to elucidate the phenomena of physiology connected with these actions.

An important distinction exists between animals and vegetables, in the mode in which they receive their nourishment. Vegetables are constantly absorbing matter from the soil: it immediately passes into the general sap-vessels, and is soon changed by respiration and secretion. Animals, on the contrary, with very few exceptions, take in food at intervals, and retain it in their stomach for a considerable time, where it undergoes a chemical change. It is this which constitutes the function of digestion, the first step in the general process by which animal matter is formed.

In the process of digestion, the food is subjected to a temperature usually above 90 of Fahrenheit; it is mixed with the gastric juice, a liquor secreted by the glands of the stomach, and is made to undergo a moderate and alternate pressure, by the contraction of the stomach itself. It is thus converted into a soft uniform mass of a greyish colour, in which the previous texture, or nature of the aliment, can be no longer distinguished.

In the production of these changes, the gastric juice appears to be the principal agent. It has been proved by the experiments of Stevens, Spallanzani, and others, that it possesses a real solvent power, or that, independent of any heat or pressure, and even out of the body, it is capable of dissolving animal and vegetable matter. At the same time, these circumstances must promote its action, and they must therefore be assistant causes in the process of digestion. In the graniverous animals, trituration especially, from the action of the stomach, has a very important share in reducing the food to that state in which it is more easily acted on; while in carnivcrous animals, which have a membranous stomach, the effect is produced almost entirely from the action of the gastric fluid.

It has often been observed, that whatever may be the kind of food, the pulpy mass into which it is resolved in the stomach is in appearance nearly the same. The nature of the change which it suffers, has been by no means well ascertained. It does not seem to be resolved into its ultimate principles, from which new combinations are formed. The soluble parts of the vegetable and animal food, the mucilage, fecula, sugar and oil, of the one, the gelatin, albumen and other principles of the other, are rather only separated from the insoluble parts of each, and brought into a state of intimate mixture with each other, so as to be more readily acted on by the other chemical powers to which it is to be exposed. It is at the same time partially animalized by the mixture of the saliva, and gastric juice, by which probably its further assimilation is facilitated.

The chyme, as this pulpy mass into which the food in the stomach is resolved is termed, passes by the pylorus into the intestinal canal, where it is mixed with the pancreatic juice, and the bile, and is still exposed to the same temperature and alternating pressure. The thinner parts of it are absorbed by the slender tubes termed the Lacteals: the liquor thus absorbed is of a white colour: it passes through the glands of the mesentery, and is at length conveyed by the thoracic duct into the blood.

This part of the process is termed Chylification, and the white liquor thus formed Chyle. It is an opaque milky fluid, mild to the taste. By standing for some time, one part of it coagulates; another portion is coagulated by heat.

We know little of the nature of the changes which constitute Chylification. Some have supposed that the bile, or some part of it, combines with part of the food, and animalizes it; while others suppose it to be only an excrementitious fluid, and to be useful in nothing but in stimulating the intestines to action. Neither opinion has been proved, though the former seems more probable than the latter, from the large quantity of bile secreted, compared with the quantity discharged from the intestines. We know still less of the changes which the chyle suffers in its passage through the mesenteric glands; but by the general process it is evident, that it is assimilated to the nature of animal matter, as it possesses the property of albumen, of being coagulated by heat.

The chyle, after mixing with the lymph conveyed by the absorbent vessels, is received into the blood which has returned from the extreme vessels, and before it passes to the heart. All traces of it are very soon lost in the blood, as it mixes perfectly with that fluid. It is probable, however, that its nature is not immediately completely altered. The blood passing from the heart is conveyed to the lungs, where it circulates over a very extensive surface presented to the atmospheric air, with the intervention of a very thin membrane, which does not prevent their mutual action. During this circulation, the blood loses a considerable quantity of carbon, part of which, it is probable, is derived from the imperfectly assimilated chyle, as this, originating in part from vegetable matter, must contain carbon in larger proportion than even the blood itself. In the process of respiration, we have also reason to believe, as I shall soon have to observe, that a portion of oxygen and another of nitrogen are received, which enter into the composition of the blood.

The process of sanguification, however, is probably not yet completed. The blood returning to the heart, is distributed over the whole body. In the extreme vessels it undergoes a certain change, is converted from the arterial to the venous state, and though this is connected with the different species of secretion, yet it is probable also, that in these vessels the process of animalization is finished. There remains, as the result of it, a redundance of carbon; and the venous blood is again brought back to the heart, and conveyed to the lungs, where this excess of carbon is discharged.

If we now examine the composition of the blood, we find it to be entirely different from that of vegetable matter, from which it is ultimately derived. It is a heterogeneous fluid, composed of various principles which we can easily distinguish, and which all possess the general characters of animal matter.

From this fluid the solids seem directly to derive their nourishment, by attracting immediately the principles which it contains ready formed; for there is perhaps no solid in the animal body, of which not merely the ultimate, but even the immediate principles exist in the blood.

There is another process, however, that of Secretion, by which new products are formed. In the course of the circulation, the blood is conveyed to certain organs named Glands, and is there entirely changed in its chemical composition, so as to form various products not pre-existing in the mass of blood, and which form some of the most important varieties of animal matter.

Various hypotheses have been given of the nature of this process. At one time it was regarded as merely mechanical, as a species of filtration; but the mere fact, that the products are entirely different from any existing in the blood, afford a sufficient refutation of this opinion, while it proves it to be strictly chemical. A fluid is received into certain vessels; in these its composition is changed, not merely from the abstraction of principles previously existing in it, but from new combinations of its elements. From the mere description of this process, therefore, it is evident, that it consists of a series of chemical actions.

But if we further endeavour to investigate how these are effected, or inquire particularly by what powers these new chemical compounds are formed, we find ourselves engaged in a task of the most difficult kind. In the structure of the glands we perceive nothing but a series of convoluted vessels, through which the blood circulates, and we are unable to discover, how the action of these vessels can operate so as to form one new product; far less, how different glands can, from the same fluid, form substances entirely different in their chemical composition and properties.

Some physiologists have sought to solve this difficulty by saying, that secretion is the effect of the vital power of the secreting organ; not aware, perhaps, that this is affording no explanation, but merely acknowledging an occult cause. Digestion was, for a time, ascribed by those who were dissatisfied with the hypothesis of fermentation or of mechanical trituration to vital action; and the production of animal heat was referred to the same cause. We now know, that these are the effects of processes strictly chemical. We have every reason to consider secretion in a similar point of view; and it is sufficiently probable, that future investigations may ascertain its nature, as satisfactorily as modern chemistry has discovered the cause of what must at one time have appeared as difficult, the production and regulation of animal temperature.

It might be supposed, as one mode of solving these difficulties, on chemical principles, that the matter of which the gland itself consists, exerts an attraction to one or other of the elements of the blood, by which the order of attractions being broken, new products may be formed. But the obvious objection to this opinion is, that the glandular matter must undergo a proportional change; a change utterly incompatible with the office it was designed to perform, or even with its existence as an organized part.

On a subject so obscure, it is impossible to give more than hypothesis; and even that can be supported by little direct proof. Yet if it afford any tolerable explanation of the phenomena, it is always advancing one step, and may give rise to new views. It may perhaps be supposed, that the cause productive of the new combinations which constitute secretion is the simple approximation of the elements existing in the blood. That fluid is propelled by a *vis à tergo* into canals of the most astonishing minuteness, the diameters of which are still farther diminished, from their alternate contraction from the stimulus of the blood. There can be no doubt, that, in compounds, the force of attraction subsisting between their constituent particles is modified by the distances at which these are placed; and in compounds especially which consist of four or more principles, the slightest alteration in their relative situation is sufficient to change entirely their existing attractions, and induce new combinations. The blood is a compound of this kind: its ultimate principles, too, are capable of entering into an innumerable variety of combinations with each other. We may conceive, therefore, that, when subjected to the contraction of the extremely minute vessels through which it is forced to circulate, the relative positions of its elements will be changed, their attractions will of course be altered, and new combinations formed. And if we suppose a fluid thus passing through tubes of different diameters, and undergoing successive decompositions, we may easily conceive, that very different products may be formed from the same original compound.

This affords a very simple view of the nature of secretion. No complicated apparatus is requisite for the performance of the mere change, all that is necessary being the propulsion of the blood through extremely minute vessels, capable of contraction. It has accordingly frequently been observed, that new products are in different cases formed without the intervention of glands; such is the formation of the fat, of the solid fibre, and of various other parts. It is easy to conceive, that the formation of these may take place in the extreme vessels, where these products are deposited; and, in like manner, in the mere course of the circulation, may be formed the gluten, albumen, and other principles of the blood itself.

It is easy also to account for the variations to which secretion is liable, as the contractions of the vessels must vary, from variations in the state of their irritability, or of the stimuli which may be applied to them.

From secretion a variety of products are formed, as the bile, milk, fat, the bony matter, the matter of membranes, and a variety of others. These complete the formation of animal matter, and comprehend its several varieties.

Such are the different steps of the process of animalization. The food is digested in the stomach, mixed with animal matter in the intestine canal, and converted into chyle. This mingles with the blood, loses a portion of carbon in the lungs, and perhaps receives some oxygen and nitrogen: in the extreme vessels it is finally converted into the general principles of animal matter, and, in the glands, is converted into various secreted products.

Since the different varieties of animal matter are thus ultimately formed by the processes of digestion and respiration, it becomes an object of inquiry, whether, from the principles known to be conveyed by these processes, we can explain their formation. Their ultimate elements are carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus, with minuter portions of lime, iron, potash, and soda. Are these, or any of them, formed by the animal system, or are they merely introduced into the body from without, and brought into new combinations?

With respect to this question, so far as it regards the three first of these substances, carbon, hydrogen, and oxygen, there can be no difficulty. They exist in vegetable matter in a proportion even larger than that in which they exist in the animal products; and it is evident, therefore, that they are conveyed by the food.

To trace the origin of the nitrogen in the animal system is more difficult. It exists in small quantity in vegetable matter, and only in some varieties of it; and as many animals live entirely on vegetable food, and almost all may be brought to live principally on it, it is far from being evident whence the nitrogen so abundant in the composition of both their solids and fluids is derived.

It has been supposed to be received in respiration. Dr Priestley, in endeavouring to determine the chemical changes which the air suffers in that process, found reason to conclude, from his experiments, that an absorption of nitrogen took place; and a similar conclusion appeared to be established by the experiments of Goodwyn. On the other hand, Lavoisier inferred from his experiments, at an early period, that the absolute quantity of nitrogen in the air received into the lungs remained unchanged. Mr Davy, in the course of his researches on the respiration of nitrous oxide, observed a diminution in the quantity of nitrogen air in the atmospheric air in ordinary respiration, and, as is afterwards to be more fully stated, concluded, that about five cubic inches of it disappear, or are absorbed by the blood, in the course of a minute. And this consumption of nitrogen appears since to have been established by the experiments of Pfaff [*]. This affords an abundant source whence all the nitrogen found in the animal system may be derived. It may be remarked, however, that the fact has been doubted by some physiologists; and it is not impossible that this nitrogen may have a different origin. It has been inferred, that vegetable substances contain none of this principle, as they in general afford no ammonia in their decomposition by heat; but if it be an element in the composition of acetic acid, as appears to be established, since this acid is one of the usual products of that decomposition, this inference will require to be corrected; and a sufficient quantity of nitrogen may perhaps be contained in the vegetable matter used as food, to afford, by accumulation in the system, all that exists in animal matter. In all our researches on questions similar to this, it is also to be recollected, that the substances which we at present regard as simple may be compound; and that, with regard to the present case, nitrogen may either be a compound substance, or may exist in the composition of others, which our imperfect knowledge ranks as elementary.

Phosphorus is another substance which exists in sparing quantity in vegetables, and is contained much more abundantly in animal matter. Its origin is not less obscure. Some have supposed, that it is a product of animalization; which appears not improbable, when we consider not only the proportion of phosphorus which exists in the solids that constitute the animal fabric, but farther, the large quantity of phosphoric salts which are discharged as excrementitious. It appears, indeed, that a considerable proportion of it is contained in those varieties of vegetable matter which are chiefly subservient to animal nourishment. Vauquelin, as has been already remarked, found it in the farina of wheat, constituting, probably, an element in the composition of the gluten: the ashes of one pound of wheaten flour yielded about 84 grains of phosphate of lime; whence he has calculated, that a person taking one pound of this flour daily, would, in the course of one year, receive 3 lbs. 6½ ounces of this salt. Many animals, however, live on food in which the existence of this principle has not been established, those, for example, which feed on grass; at the same time, it is to be remarked, that the urine of these animals contains no phosphoric salts. An accurate analysis of the vegetable nutritious substances, with a comparison of the composition of the solids and fluids of the animals which feed upon them, are still wanting to throw light on this subject.

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[*] Annales de Chimie, tom. lv. p. 177.

The same difficulties exist with regard to lime and iron, the two principal remaining substances which enter into the composition of animal matter. There can be no doubt, however, but that both of them are found in almost all the vegetable products; and lime is contained in every kind of water which can be used by animals as drink. Yet facts have also been stated, in proof that they are formed in the process of animalization. The strongest, perhaps, is derived from the analysis by Vauquelin of the eggs of a hen, compared with the food which the animal received, from which it followed, that the quantity of phosphate and of carbonate of lime discharged was greater than what was contained in the food * ; whence it followed, that both lime and phosphorus had been generated in the animal system. Others which have been stated are less conclusive : the argument drawn from the large quantity of calcareous matter secreted by certain marine animals, to form their shells, is evidently so, as a large quantity of lime in a state of combination exists in sea-water. And the experiments which have been stated to prove, that an egg, previous to incubation, contains less lime and less iron than the chick does immediately after it is hatched †, are too inaccurate to admit of any certain conclusion. This applies indeed, perhaps, to nearly all the researches on this subject. The general fact, that the greater part of those substances used as food by animals contain these principles, is perhaps sufficient to justify the belief, that they are introduced into the body, and not actually formed ; any analysis by which the question might be determined with more precision being liable to such difficulties and sources of fallacy, that, as hitherto executed at least, it can afford no certain conclusion.

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* Annales de Chimie, tom. xxix. p. 22.

† Abernethy, Physiological Essays.

CHAP. II.

OF THE ANIMAL PRODUCTS.

THE animal, like the vegetable products, may, to a certain extent, be reduced to a certain number of species or proximate principles, characterised by certain distinctive characters. Yet this classification is much less perfect than it is with regard to vegetable matter: we are far from being able to place under it the various animal solids and fluids; and we are therefore, in the present state of animal chemistry, rather compelled to give the history of these solids and fluids in the state of composition in which they exist, introducing under them the description of such proximate principles as have been sufficiently defined. Under this arrangement, the history of the blood, the common source whence the varieties of animal matter are derived, must first be given, and is of much importance, as this fluid contains, already formed, the three most common principles, albumen, gelatin, and fibrin. From the history of the blood, we proceed to that of the other fluids and solids, in that order best adapted to their various relations.

SECT. I.

OF THE BLOOD.

Blood, that fluid which circulates through the vessels of the animal system, sustains life, and affords the principles whence all its products are formed, varies considerably in its qualities, in the different orders of animals. In insects and some others, it is white or pellucid; in the more perfect animals it is of a red colour. Its consistence is somewhat thick, and it has a saponaceous feel: it has a sweetish slightly saline taste, and a perceptible odour, more or less strong in different animals. Its specific gravity is from 1.03 to 1.05. It is miscible with water, and is coagulated either by heat or cold.

Though blood, as it circulates in the body, appears to be a homogeneous fluid, it appears under the microscope to be heterogeneous, or presents the appearance of particles of a globular form, diffused through a liquid. On being removed from the body, in a short time too, the apparent uniformity of its composition is subverted: it separates into a fluid of a yellowish colour and slight tenacity, and into a coagulum more or less firm, of a dark red colour. This process is the Coagulation of the blood: the fluid part is the Serum, the solid the Clot or Crassamentum. By a further examination, the latter is likewise found to be a mixture or very slight combination of two principles,—of a red colouring matter, soluble in water, and, therefore, abstracted by washing the crassamentum; and of a white, solid, elastic, and fibrous matter, which remains. The former has been named the Colouring Matter, or the Red Globules of the Blood; the latter the Gluten or Fibrin. The proportions of all these to each other, vary considerably in different animals, and in the same animal in different states of the system.

The cause of that spontaneous change of the blood which constitutes its coagulation, is far from being well ascertained. Though it is retarded by motion, and by a moderate temperature being kept up, in other words, takes place more readily when the blood is at rest, and when the temperature is allowed to fall below the natural heat of the blood itself; yet it also takes place under the opposite circumstances, when it is agitated, and when its temperature is not reduced. Neither is the access of atmospheric air necessary, as the coagulation takes place *in vacuo*, as Mr Hunter ascertained. Experiments have been stated, particularly by Luzuriaga *, which seem to prove, that the coagulation takes place much more rapidly when the blood is exposed to nitrogen, carbonic acid, or nitrous gas, than when exposed to oxygen or to hydrogen gas. These facts seem quite anomalous, and point out no principle: and it has been affirmed by Mr Davy, that when blood is exposed to these and other gases, there is no marked difference in the times of coagulation †.

Since the above circumstances have so little share in the coagulation of the blood, some have ascribed it to the evolution of some gas, which, while it remained in the vessels of the animals, was retained by pressure, and this, escaping from the fibrin, disposed it to coagulate. But this is confirmed by no fact.

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* Dissertatio Inauguralis, Edin. 1786.

† Researches on Nitrous Oxide.

The spontaneous decomposition of the blood in its coagulation, affords the easiest method of discovering its immediate or proximate principles; and from our knowledge of these, we are better enabled to determine the nature of the changes which re-agents produce on the entire blood itself. These principles, therefore, are first to be investigated.

The liquid formed by the coagulation, the Serum, as it is named, is a fluid slightly viscid and consistent, of a pale yellowish colour, and an insipid somewhat saline taste. Its specific gravity is about 1.028. It mixes readily with water in all proportions, losing, with a large proportion of water, its colour and taste. It is slightly alkaline, as it renders the syrup of violets green: this alkali, Rouelle discovered to be soda; and muriate of soda is obtained, when muriatic acid has been added to serum, and the liquid evaporated.

When the serum is exposed to a moderate heat, it coagulates, or forms a kind of consistent mass more or less firm, but still tremulous, with a portion of interposed fluid. This coagulation takes place at a temperature of 160°, and it does not require the presence of the air. It is quickly produced, by adding to the serum two or three parts of boiling water; but if the serum has been previously much diluted with cold water, it does not happen. It is also occasioned by the addition of a number of substances, as by several acids, by salts having an excess of acid, by alkohol, and by several metallic oxides.

This coagulation, especially as it is produced by heat, is a true analysis of the serum. As the substance which coagulates has all the properties of the white of an egg, it has been termed Albumen. It exists in many other animal products, and is indeed one of the most abundant proximate principles of animal matter, especially of the animal fluids and of the softer solids; it is therefore necessary that its properties should be fully examined.

Albumen, then, (of which the white of the egg furnishes us with the best example), is distinguished by the following properties.

It is soluble in water, and is again separated from it by coagulation, by the application of heat, by alkohol, by acids, and several metallic oxides. After its coagulation, it is no longer soluble in water, unless by long boiling. It has been observed, that the coagulum separated by alkohol, is more soluble than that separated by acids; the acid probably, while it precipitates the albumen, affording it a small portion of oxygen. It has been supposed by Fourcroy even, that the separation of this principle is always owing to its receiving oxygen; but the fact, that it is precipitated by alkohol, while it is not by several substances containing much oxygen and yielding it readily, as the oxymuriate of potassa, the black oxide of manganese, and some others, sufficiently refute this opinion: nor is the cause of the coagulation of albumen well ascertained; but it appears from the change it suffers at the same time in its properties, to be owing to some change in the combination of its principles. If albumen is dissolved in 8 or 12 parts of cold water, it is not coagulated by heat; but when diluted even with a large quantity, as with 1000 times its weight, the liquor when heated, though not properly coagulated, becomes opaque *.

Albumen is dissolved by the alkalis. Its solution by ammonia proceeds very slowly, and is completed only in the course of several months. The solution is in the form of a viscid pulp, very porous, and of a much greater volume than the original albumen.

Pure potash or soda dissolves it with facility even in the cold: a quantity of ammonia is disengaged during the solution; a grey powder is precipitated, and the liquor is of a dark brown colour.

Acids dissolve albumen. In the concentrated sulphuric acid, the solution goes on slowly, and is completed in a few days. In the nitric acid the mutual action is more rapid; it can scarcely, however, be termed a solution: a large quantity of elastic fluid is discharged, and an oily-like matter is precipitated, soluble in alkohol.

Albumen, when decomposed by heat, affords the usual products of animal matter. It also contains a portion of sulphur. The effect of the white of an egg in blackening silver, has been long known; and Parmentier and Deyeux found, that on triturating albumen with a solution of silver, and digesting it in water with a gentle heat, sulphuret of silver is formed. Its residuum affords phosphate of lime.

In the analysis of animal matter, it is of considerable importance to have tests, by which minute quantities of albumen may be detected, as it enters largely, as an immediate principle, into the composition of many animal pro-

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* Bostock, Nicholson's Journal, vol. xi. p. 247.

ducts. The corrosive muriate of mercury is one of the most delicate, and at the same time the most accurate. If a very small portion of the albumen of an egg, which has been previously mixed with two parts of water, be added to a large quantity of water, on adding a few drops of the solution of the corrosive muriate, a milkiness, and at length a precipitate, is occasioned. Dr Bostock found, that by this test, albumen diluted with 2000 times its weight of water, was detected. The acetite of lead, (Goulard's extract), and the nitrate of silver, likewise precipitate it, but they are not such useful tests, as they act also on other varieties of animal matter, which the muriate of mercury does not *. A solution of tannin produces with it, slowly, a yellow precipitate.

When albumen has been coagulated, its properties, as has been already remarked, are considerably changed. It is no longer soluble in water: by drying it becomes brittle, hard, and semi-transparent, as Mr Hatchet, who has examined it in this state †, has remarked. Digested in water, it becomes soft, but it does not soon suffer any further change. It is changed by the action of the acids. Nitric acid, in particular, appears, from Mr Hatchet's experiments, to convert it into a matter analogous to gelatin. The alkalis dissolve it, at the same time decomposing it and causing a formation of ammonia.

Albumen, as has been remarked, exists not only in the blood, but forms a constituent part of many of the soft solids. From Mr Hatchet's experiments, it appears to

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* Nicholson's Journal, vol. xi. p. 247.

† Philosophical Transactions, 1800, p. 376.

form the basis of cartilage, shell, horn, and hair, and it enters into the composition of membrane, muscular fibre, and bone.

If the coagulated mixture, obtained by the action of heat on serum, be gently pressed, there flows from it a liquor somewhat turbid, named the Serosity; it may be diluted with water, and rendered clear by filtration. If it be then made to boil gently, on cooling it will become gelatinous, its consistence being more or less firm or tremulous, according to the quantity of water that had been employed in its dilution.

By this experiment, then, we discover the existence of another proximate principle in serum,—of a substance which is soluble in water, and which does not separate from that fluid on being heated, but forms with it a perfect solution of a gelatinous consistence. By modern chemists, this substance has been named Gelatin, and it forms a principal part of many of the animal solids, particularly of those that are membranous. It is from its presence, that the decoctions of animal matter, when of a certain strength, become gelatinous. The skin, cartilages, tendons, and the white solids in general, are principally composed of it; and decoctions of these, when the oily matter has been separated, afford it in nearly a pure state, for the purpose of experiment. Glue, which is used in the arts, on account of its adhesive property, and is prepared by boiling these substances strongly in water, is solid gelatin; and isinglass, prepared from the membranous parts of the sturgeon, is the same principle in a pure form.

Gelatin is discovered in the serosity, not only by the property of forming a jelly by decoction, but likewise by the appearances produced by re-agents. If the infusion of galls or any other vegetable containing tannin be added, a flocculent yellow or brown precipitate is formed; and the proof that this is owing to the gelatin contained in the serum is, that the appearance is precisely the same as is produced by the addition of the same re-agent to a solution of pure gelatin. Tannin is by far the most delicate test of gelatin. One part dissolved in 5000 of water was found by Dr Bostock to be discovered by the turbid appearance, and even the precipitation, produced by the infusion *. To render it accurate, however, it is necessary to attend to the circumstance, that tannin likewise produces a precipitate with albumen. This, however, is much less evident; and the distinction between them is likewise easily established by the use of other tests. Thus, a solution of corrosive muriate of mercury, or of that form of acetate of lead known by the name of Goulard's Extract, does not affect gelatin, while it renders the solution of albumen immediately turbid.

The proportion of this principle which is necessary to give to water the gelatinous consistence, appears to be less than one part of gelatin to 150 of water. Even when the consistence is most firm, the whole becomes liquid when the temperature is raised, and again gelatinates as it cools.

Alkohol precipitates the gelatin from the serosity, but on heating the mixture sufficiently, the gelatin is re-dissolved.

The acids dissolve gelatin readily, and, at the same

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* Nicholson's Journal, vol. xi. p. 250.

time, decompose it. Nitric acid disengages a portion of nitrogen, less considerable, however, than what is yielded by some other animal substances from the same treatment: oxalic acid is at the same time formed, with a little oily matter. Sulphuric acid chars it. Oxymuriatic acid, transmitted in the state of gas through a solution of it in water, converts it into a white concrete matter, not soluble in water, and which Lagrange considered as gelatin oxygenized *.

The alkalis dissolve gelatin. The solutions of barytes, lime, and strontites, produce in its solution a milkiness, owing, according to Fourcroy, to the precipitation of phosphate of lime. Some of the metallic oxides communicate oxygen to it; and a number of the metallic salts cause precipitates to fall from its solution.

Gelatin is decomposed by heat. It affords carburetted hydrogen and carbonic acid gases, carbonate of ammonia, and empyreumatic oil, the residual charcoal containing phosphate of lime. It is very liable to putrefaction.

If the liquor remaining after the albumen and gelatin have been separated from the serum be examined, it is found to be little more than a solution of certain saline substances. Of these the principal is soda; and as no effervescence is produced on the addition of anacid, it is concluded to exist in the serum pure, or not combined with carbonic acid. Muriate of soda, phosphate of soda, and phosphate of lime, appear likewise to exist in the serum in smaller quantity, and are discovered by the precipitates produced, by peculiar tests, and particularly by the

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* Nicholson's Journal, vol. xiii. p. 209.

nitrates of silver and mercury. When a solution of nitrate of mercury is added to it, a red-coloured precipitate is formed, which, according to Fourcroy, is principally phosphate of mercury.

Such, then, is the composition of the serum of the blood, as indicated by a very simple analysis. It is composed of two distinct principles, albumen and gelatin, dissolved in water, which likewise holds in solution pure soda, with muriate and phosphate of soda, and phosphate of lime.

From the composition and properties of these several products, we perceive the nature of the changes which the serum exerts upon certain chemical agents, or suffers from them. Thus, from the soda it contains, it changes the vegetable colours to a green; it gelatinizes from evaporation; it is coagulated by heat, by alkohol, and acids, from the coagulability of the albumen; it is rendered thinner by the alkalis, from the solvent power they exert on the albuminous matter; gives a copious precipitate with tannin, from the combination of that principle both with its gelatin and albumen; it reduces several of the metallic oxides when digested with them, and passes itself to the solid state,—a change probably owing to its albumen attracting oxygen; it putrefies on exposure to heat, from the spontaneous decomposition of its principles, especially of its gelatin, which is even more disposed to putrefaction than the albumen. And when decomposed by heat, it affords carbonate and prussiate of ammonia, with an empyreumatic oil, carburetted and sulphuretted hydrogen gases, with carbonic acid gas; its residuum being charcoal, containing the salts which have been already mentioned as being dissolved in this fluid.

The properties of the Crassamentum, or solid coagulum of the blood, are next to be considered.

This is of a dark red colour: by exposure to atmospheric air, or to oxygen, it acquires a more florid red hue, and, on the contrary, it becomes much darker on being exposed to hydrogen, carbonic acid, or indeed any other gas, carburetted hydrogen excepted, which like oxygen gives it a more vivid colour. In all these cases, the gas by which the change is effected seems to be absorbed, though not in any considerable quantity. These changes take place, even when the coagulum is covered with serum. The change of colour is confined nearly to the surface; the crassamentum, when rendered florid by exposure to oxygen, appearing of a dark colour internally, when it is cut into.

The crassamentum exposed to the air does not immediately putrefy: it retains its colour and consistency for several days, if the temperature of the air is not high. If it be exposed to a moderate warmth, it is dried: it retains its dark red colour, and, if kept in a dry place, may be preserved for a long time without decomposition.

The coagulum still retains in its substance a quantity of serum, which gives it particular properties. Thus, if it be thrown into boiling water, it renders the water opaque, from the coagulation of part of the albumen of the serum: from the same cause, its consistence is increased by digestion in alkohol, or by the affusion of acids, while the alkalis soften and dissolve it. Nitric acid dissolves it, and renders it black.

The crassamentum, exposed to heat, affords the same products as other animal substances; and the charcoal, which is the residuum, contains a quantity of iron, with salts having lime and the alkalis for their bases, and containing phosphoric acid.

After noticing these general properties of the crassamentum, it is to be observed, that it is not a homogeneous substance, but consists of two principles mixed together, or very slightly united. These are easily separable. If the crassamentum is washed with water, by inclosing it in a linen bag, immersing it repeatedly in water, and, at the same time, pressing it gently, the water acquires a deep red colour, and there remains a fibrous matter, nearly perfectly white.

By this simple analysis, then, the crassamentum is resolved into two distinct principles,—a colouring matter, carried off by the water, and another solid fibrous substance, which remains. The former is named the Colouring Matter of the Blood, or Red Globules; the latter, the Gluten, Coagulable Lymph, or now more generally the Fibrin.

The colouring matter, from microscopical observations, has been supposed to consist of round globules, which some have even imagined to be organized. It is soluble in water, but, after some time, a deposition takes place from this solution. At the temperature of 170°, it likewise loses its colour, and brown flocculi are deposited.

This matter seems to be that upon which the gases act with peculiar energy. If it is exposed to atmospheric air, or oxygen, or even to substances capable of affording to it oxygen, if, for instance, oxide of mercury is diffused through its watery solution, it acquires a florid hue: if exposed to hydrogen or carbonic acid, it is said to become of a brown or dark red colour. I have not observed, however, any change of colour by passing through it carbonic acid gas.

The coagulum formed from the crassamentum by the heat of a water-bath may be dried, so as to be rendered brittle and pulverulent. Alkohol digested on it in this state dissolves a small portion, and assumes a red colour. The acids, if added to the soft crassamentum, darken it, and produce a partial coagulation. The alkalis dissolve it. From these properties, it appears to approach to albumen, with which some principle is combined, communicating to it colour.

This principle has been recognised to be iron. The existence of this metal in the blood had been known to chemists. Menghini discovered, that from blood dried by a very gentle heat, it could be extracted in a magnetic state. Bucquet found, that the colouring matter separated from the crassamentum, dried and decomposed by heat, gave a residuum, the colour of which depended on iron. Sage supposed, that the iron existed in the blood in combination with phosphoric acid; and Fourcroy and Vauquelin have given experiments, by which they suppose this to be established. If the colouring matter obtained from its solution in water be decomposed by heat, a residuum of a dark red colour is obtained, amounting to 0.0045 of the blood employed, and which contains some foreign matter besides iron. If this residuum be digested in nitric acid, a part of it is dissolved, leaving another part more red than before. Ammonia poured into this solution affords a white precipitate, which when treated while wet by pure potassa, loses weight, and assumes a dark red colour;

and lime-water added to this alkaline solution forms a precipitate of phosphate of lime. To understand, continues Fourcroy, how the phosphate of iron which this analysis shows exists in the blood is in a state of solution, by means of the soda which that fluid likewise contains, it is necessary to remark, that this compound may exist in two states; the one, the neutral phosphate, of a grey colour, pearly, insoluble in water, and soluble in acids,—the other, sub-phosphate, or phosphate with an excess of base, of a brownish red colour, less soluble in acids, but soluble in alkalis. It is in this latter state of phosphate supersaturated with oxide of iron that it exists dissolved in the blood,—a state in which it is maintained by the action of the soda. These chemists accordingly found, that this sub-phosphate of iron is dissolved in the serum of the blood, or in the white of an egg, even without heat, and that it forms a strong red colour similar to that of the blood. A little pure alkali accelerates this solution, and renders its colour more perfect and lively *. The principles contained in the colouring matter of the blood seem to exert a considerable action on metallic oxides. Vauquelin found, that copper was very easily dissolved by it.

According to the view now given, the colouring matter of the blood consists of albumen, with perhaps a portion of gelatin, united with soda, and sub-phosphate of iron. From its decomposition by heat, there are also obtained some other saline matters, principally phosphates

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* System of Chemical Knowledge, vol. ix. p. 208.

and muriates, which are probably, however, not very essential to its composition.

The Fibrin is the white solid matter that has formed the basis of the crassamentum, and from which the colouring matter is carried off by washing. It can also be obtained from the general mass of blood itself, by agitating it with a stick in an open vessel: the other principles are intimately mixed together, and the fibrin adheres to the stick. It also forms those concretions named Polypi, which are found in the vessels of animals after death; and in certain diseases, it is disposed even in a very short time to separate from the other principles, when it gives rise to the appearance named the Inflammatory Crust, or Buffy Coat. It is it which gives to the blood the property of coagulating spontaneously. It is contained in it in considerable quantity, amounting, according to Fourcroy and Vauquelin, at a medium, to 0.0028, though the proportion varies considerably. It is also contained in many other of the animal products, as in the muscular fibre, of which it forms the basis, and is one of the best defined proximate principles of animal matter.

Fibrin is a solid white substance, free of taste or smell, and of a fibrous texture, as is discovered by the microscope, tough, and somewhat elastic: it hardens and contracts much, on exposure to a very moderate heat, and becomes wrinkled like parchment. It is entirely insoluble in water, except at such a high temperature as that which is obtained by pressure in Papin's digester. Moistened with water, it very soon softens, swells, and begins to putrefy: it suffers a similar change in a damp atmosphere. This, however, applies only to the fibrin of blood, which has probably some other matter attached to it: for Mr Hatchet found, that fibrin obtained by repeatedly washing, and even boiling the muscular fibre with water, is not very liable to putrefaction.

Fibrin is dissolved by the alkalis, but is at the same time decomposed. Pure potassa or soda acts upon it readily, even at the common temperature of the atmosphere, and forms a kind of soap: vapours of ammonia are disengaged, and a greyish matter is precipitated, which is carbonaceous. Ammonia requires a temperature equal to 170°, to enable it to act on the fibrin; it then dissolves it with facility.

The acids exert a considerable action upon fibrin. Muriatic, acetic, and several of the vegetable acids, dissolve it; the solution is decomposed by the alkalis, and even by water; but the precipitate has no longer the properties of the original matter, being, in particular, soluble in water. The sulphuric acid decomposes it, and throws down a carbonaceous powder, and forms acetic acid. Nitric acid, diluted with a large quantity of water, disengages from it a large quantity of nitrogen gas, which proceeds entirely from the fibrin, as it was ascertained by Berthollet, who first observed the phenomenon, that the acid is not decomposed. The residuum, in this case, is principally oxalic acid, with a small portion of malic and acetic acids, and a portion of fatty matter. When the nitric acid is undiluted, it suffers decomposition, and nitrous gas, mixed with nitrogen, is disengaged. The action of nitric acid, however, on fibrin, is much diversified, according to its dilution and state of concentration. If the action be slow, the fibrin, as Mr Hatchet found, passes into a state somewhat analogous to gelatin *. If heat is applied, prussic acid is formed: and in this case too it appears, from the experiments of Fourcroy and Vauquelin on muscular fibre, to be afterwards stated, that a peculiar principle, yellow, bitter, and acrid, is also formed.

Fibrin, exposed to heat, is soon decomposed. An empyreumatic oil, of a very offensive smell, first distils over, which is followed by carbonate of ammonia, and very fœtid gases, which are probably triple compounds of hydrogen with nitrogen and phosphorus: a charcoal remains, dense and brilliant, difficult of incineration, and containing phosphate and carbonate of lime.

The three principles which have now been described as existing in the blood,—albumen, gelatin, and fibrin, and which enter so largely into the composition of animal matter, have a resemblance in their properties and also in composition; but, with regard to both, they are still easily distinguished. Thus, with respect to properties, independent of other material differences, there is one simple character which serves to distinguish them, drawn from the manner in which they are acted on by water: gelatin is soluble in cold water: the solution, when evaporated, becomes gelatinous; and if this jelly be dried, it is still again equally soluble. Albumen is likewise soluble in water, but whenever the temperature is raised to 170°, it separates by coagulation, and this coagulum is not again soluble. Fibrin is clearly distinguished, by being entirely insoluble in water, at any temperature, under a com-

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* Philosophical Transactions, 1800, p. 391.

mon atmospheric pressure. The modes in which these substances are acted on by the acids, alkalis, and other chemical agents, are also entirely different.

These three principles likewise differ in their composition; for though they seem to consist of the same ultimate principles, of nitrogen, hydrogen, oxygen, carbon, phosphorus, and perhaps sulphur, yet these differ at least in their proportions. The difference seems to be principally in the proportion of nitrogen. When treated by nitric acid, gelatin is found to yield the smallest proportion of nitrogen gas: albumen more; and fibrin a quantity considerably larger than either. It seems, therefore, to be the most animalized product. It appears also to contain the largest quantity of carbon, as the charcoal left in its decomposition by heat is more abundant, according to Mr Hatchet's observation, than that from albumen or gelatin. Sulphur seems peculiar to the composition of albumen.

After thus pointing out the immediate principles of which the blood is composed, it remains to state the chemical properties of the entire fluid. These are of course derived from these principles, and from our knowledge of them may, in general, be easily understood.

Blood newly drawn, is perfectly soluble in water, or it can be diffused through it without any alteration, and this dilution prevents its spontaneous coagulation. If the mixture, however, be heated, flakes separate, consisting of the albumen, and the colour is changed to a brown. The liquor, separated from the coagulum, yields, according to Fourcroy, a yellow bitter matter, by evaporation.

Acids added to blood, immediately decompose it; they render its colour darker and brown, and produce coagulation. The nitric acid disengages nitrogen gas; the oxymuriatic acid renders it perfectly black.

The alkalis, instead of coagulating the blood, render it more thin and liquid, and prevent its spontaneous coagulation, evidently from their solvent power on the albumen and fibrin.

The neutral salts frequently alter the colour of blood, and a number of them retard its coagulation. The metallic salts, in general, decompose and coagulate it: alkohol, and even some of the vegetable principles, as starch and gum, likewise produce coagulation: tannin thickens it and renders it black.

When the watery part of the blood is withdrawn by gentle evaporation, a mass is obtained of a dark brown colour, which, if kept in a humid state, soon passes into putrefaction, and evolves very offensive products. If dried more thoroughly, it is obtained in the state of a black powder, somewhat unctuous, and which in a dry atmosphere may be preserved with little alteration. When exposed to heat it softens, swells, and in the open air inflames feebly, exhaling a very fœtid smoke. The products in this decomposition are, according to Fourcroy, first an ammoniacal liquid; secondly carbonate of ammonia, and a dense fœtid vapour, oily and inflammable: after these the vapour of prussic acid is recognisable by its smell, and lastly phosphoric acid. The residuum consists of oxide of iron nearly reduced, and perhaps in the state of carburet, phosphate of lime and muriate of soda.

When the decomposition of the blood by heat is performed in close vessels, there first distils over a quantity of water of a faint odour, and which very soon becomes putrid; when urged by a stronger heat, a liquid holding dissolved carbonate of ammonia mixed with oil: this oil comes over more copiously as the decomposition proceeds, is thick, of a dark colour, and fœtid; it is accompanied and followed by carburetted and sulphuretted hydrogen gases. The coal which remains in the retort is spongy, of a brilliant semi-metallic appearance, and difficult of incineration; it contains, along with charcoal, iron nearly reduced, phosphate, muriate, and carbonate of soda, and phosphates of iron and lime.

The preceding chemical history of blood has no reference to the different states in which it exists in the animal system. It is to be observed, however, that there are such differences; that the blood in the arteries of an animal is not the same as that in the veins; and the nature of this difference is now to be explained. This includes the chemical history of the function of respiration, by which the conversion of venous to arterial blood is effected.

The blood which returns to the heart by the veins, from the extremities of the arteries, is of a dark red colour verging to purple. When received into the right ventricle, it is immediately thrown into the pulmonary artery, and is thus conveyed to the lungs. In these it circulates through extremely minute vessels, over a surface which it has been calculated is at least equal to the whole external surface of the body. During this circulation, in which it is exposed to the atmospheric air, alternately taken in and thrown out by respiration, it changes its colour, becoming of a much more florid red. It is then returned by the pulmonary veins to the left side of the heart; is thrown from it into the aorta, and distributed through the arteries over the whole body. In the arteries it still preserves its florid red hue; but, in their minute extremities, it suffers a change opposite to that which it had sustained in the lungs: it acquires the purple hue, and constitutes venous blood, which is again immediately returned to the right side of the heart. While life exists, this circle is run, and these reciprocal changes produced.

When we examine chemically the properties of arterial and venous blood, we find no other difference between them than that of colour. They contain the same principles, and are subject to precisely the same changes from chemical agents.

The mere difference of colour, however, points out some difference in their composition, though it may be too slight to be discovered by analysis; and when we examine the phenomena of respiration, which are intimately connected with the change of venous to arterial blood, we find, that such a difference must actually exist.

In respiration, a quantity of atmospheric air is received into the lungs, and retained for a short time. When expired, on examining it, its composition is found to be altered. It has lost a considerable part of its oxygen, and it contains a quantity of carbonic acid. The changes which it has suffered are inseparably connected with the conversion of the venous into arterial blood, and consequently must be accompanied with correspondent changes in the composition of that fluid.

This is the subject, then, which is to be considered,—the chemical changes produced in the blood by respiration, from which may likewise be inferred the opposite change which it suffers in the extreme vessels.

The first point to be determined on this important subject is the changes which the atmospheric air suffers in the lungs.

Dr Black had observed, that the air expired from the lungs contains a quantity of carbonic acid, as was evident from the milkiness he found it to produce when transmitted through lime-water. Dr Priestley some years afterwards considered respiration as analogous to what he named phlogistic processes in general, that is, to processes in which oxygen is consumed; the air, in respiration, being diminished in weight and volume, and being no longer capable of supporting combustion or respiration. Lavoisier very soon after ascertained with more accuracy, by experiment, that, during respiration, the oxygen of the inspired air is in part consumed, and that, in that process, carbonic acid is formed.

When these discoveries were made, it became an object of importance to determine with accuracy the extent of these changes; in other words, the quantity of oxygen consumed, and that of carbonic acid produced. With regard to this, however, the results of the experiments of different chemists have been extremely discordant; and there are peculiar sources of fallacy to which they are subject, which it is difficult completely to obviate, the changes themselves being liable to be influenced by the state of the circulation, the nature of the food, the state of the assimilatory organs, and the temperature, all of which it is not easy to obtain uniform. The experiments, too, have often been performed in an improper manner, not on natural respiration, but on air repeatedly inspired; or even by confining an animal in a quantity of air, when there was not only this source of error, but another not less important in the effects of cutaneous transpiration.

The first experiments that were made with the view of determining the proportion of oxygen consumed, to that of carbonic acid formed in respiration, were those by Crawford and by Lavoisier. Crawford found, that when 40.86 cubic inches or 20.1 grains of carbonic acid gas were formed, 56.86 cubic inches or 18.9 grains of oxygen were consumed *; and Lavoisier obtained, by a similar experiment, a result not far different, 26 grains (English weight) of carbonic acid being produced, when 23.2 grains of oxygen were consumed †: in both cases, therefore, a larger proportion of oxygen disappearing than was necessary to form the quantity of carbonic acid expired, on the common calculation of the composition of that acid, that it consists of 72 of oxygen and 28 of carbon. The experiments, however, were made in the exceptionable manner of confining an animal in the air respired, and, for the reasons already stated, cannot therefore be relied on as indicating the proportions of the changes in natural respiration.

Dr Goodwyn, by examining the air received into the

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* Crawford on Animal Heat, p. 347.

† Annales de Chimie, tom. v. p. 264.

lungs in one inspiration, found, that when twelve cubic inches were breathed, the air expired was found to have lost 1.56 of oxygen, while it had acquired 1.32 of carbonic acid; so that when 11 parts of carbonic acid were produced, 13 parts of oxygen by measure were consumed; or, for the sake of comparison with other experiments stating the consumption of oxygen at 100, the production of carbonic acid was to the extent of 84.6 [*]. More confidence may be placed in this result, as it is free from the sources of error to which the preceding experiments are liable, though still it might be liable to some fallacy, from the small quantity of air operated on, particularly from this quantity being not the whole of what is submitted to the action of the blood in the lungs in a single respiration.

Priestley, in some experiments subsequent to those which he first made on respiration [†], found the proportion of oxygen consumed to that of carbonic acid formed still higher than the proportions above stated. He breathed repeatedly in 100 ounce measures, or 189.8 cubic inches of atmospheric air: the volume of the air was reduced to 71 ounce measures: 20.7 ounce measures, or 12.42 grains of oxygen had disappeared, and 6 cubic inches, or 4.4 grains only of carbonic acid were found in the residual air; this, according to the usual estimate, contains only 3.3 grains of oxygen, and not less than 9.12, therefore, had been farther consumed. The difference of this result with those of others, and the great diminution of the volume of the air, must render the accuracy of the experiment very doubtful; and what proves this, indeed, is, that in another experiment only 7.8 of oxygen disappeared, when 4.4 of carbonic acid were formed. Probably from the repeated forcible inspiration of the same air, a quantity of it had been absorbed, or, at the concluding expiration, the due proportion had not been thrown out from the lungs.

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[*] Connections of Life with Respiration, p. 51.

[†] Philosophical Transactions, vol. lxxx. p. 108.

In a memoir on respiration, in the Memoirs of the Academy of Sciences for 1789, by Seguin and Lavoisier, it is briefly stated, that, from experiments by the former chemist made upon himself, the mean consumption of oxygen in respiration is at the rate of a cubic foot an hour, which, in the course of twenty-four hours, amounts to 2 lbs. 1 oz. 1 dr. and that, in the same time, the quantity of carbonic acid formed is equal to 2 lbs. 5 oz. 4 dr. which gives a proportion of 100 of oxygen consumed to 112 carbonic acid formed *. But in a second memoir, in the Transactions of the Academy for 1790, a very different result is given; the consumption of oxygen by respiration is stated at a little more than 22 cubic feet in twenty-four hours, (38.413 cubic inches), or 33 ounces 1 dr. and 10 grains; while the quantity of carbonic acid formed in the same time is stated at only 8 cubic feet 6 cubic inches, or 17 ounces 7 dr. 4 grains, which is in the proportion of 100 of oxygen consumed to 51.5 of carbonic acid formed †. Such a discordance prevents much confidence from being placed in either result, and as the account given of the experiments is brief and imperfect,

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* Mémoires de l'Acad. des Sciences, 1789, p. 577.

† Ibid. 1790, p. 609.

owing to the circumstances under which it was drawn up, it is in vain to seek to reconcile them *.

The experiments of Mr Davy on this subject were made with an apparatus well adapted to measure with accuracy the volumes of the air operated on; and as they were also performed on natural respiration, they appear scarcely liable to any source of error. It follows from them, that when 31.6 cubic inches of oxygen are consumed, which is in the course of respiration for a minute, 26.6 cubic inches of carbonic acid are produced, or the consumption of the former is to the production of the latter in the ratio of 100 to 84.1 †. This result as to the proportions agrees almost precisely with that established by the experiments of Goodwyn.

Some years ago, and prior to Mr Davy's experiments, I performed some in a similar manner, of which I read an account to the Medical Society of Edinburgh ‡. A large thin varnished bladder was furnished with a stop-cock, and by a little practice I acquired the facility of inspiring *from* the external atmosphere and *into* the bladder; the stop-cock connected with it being shut at the inspiration, and being opened, by turning it with one hand while the nostrils were closed with the other, at the succeeding expiration. The quantity of air expired, amounted in thirty seconds to 265 cubic inches: by transferring a portion of it through quicksilver, and exposing it in a graduated jar, to a solution of pure potassa, the quantity of carbonic acid it contained was discovered; and from this the quantity contained in the whole expired air, when brought to the mean atmospheric pressure and temperature, was found to amount to 16.57 cubic inches. From this a small deduction must be made, for the quantity of carbonic acid gas previously contained in the air inspired; the precise amount of this it was not easy to determine, by experiment, with accuracy: but it may be supposed to be about equal to the above fractional parts, and the real quantity may be stated, therefore, at 16 cubic inches. The oxygen in the residual air, after the carbonic acid had been abstracted, was found, by various eudiometrical methods, to be equal to 17.8 in 100 parts, or to 44.1 cubic inches, the whole expired air. It remained, therefore, in order to discover what quantity of oxygen had been consumed, to discover the quantity contained in the air inspired. But as the air received into the lungs was, from the manner of making the experiment, by breathing from the external atmosphere, not measured, the quantity of it was inferred, from the quantity expired, adding to this $\frac{1}{50}$ of volume to compensate for the diminution which the air always sustains in respiration *. This makes the quantity

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* These were the last labours of Lavoisier. He fell a victim under the sanguinary tyranny of Robespierre; and he in vain requested a short time to enable him to complete these important researches.

† Researches on Nitrous Oxide, p. 434.

‡ Records of the Medical Society, for 1798.

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* It has generally been observed by those who have made experiments on this subject, that the air suffers a diminution of volume in respiration, or that the quantity expired is not exactly equal to the quantity inspired. Lavoisier stated this diminution, when the animal breathed in oxygen, at $\frac{1}{32}$, and in atmospheric air at $\frac{1}{40}$ of the volume; and Dr Goodwyn, at from $\frac{1}{50}$ to $\frac{1}{60}$, in air once respired. From a number of trials it ap-

of air inspired equal to 270 cubic inches; and this, from the analysis of the air of the room in which the experiment was made, contained 63.4 cubic inches of oxygen. But the expired air contained only 44.1 cubic inches, and consequently 19.3, or, making allowance for the correction requisite to bring it to the standard atmospheric pressure and temperature, 19 cubic inches of oxygen had been consumed. It follows, therefore, from these experiments, that in the course of a minute 38 cubic inches of oxygen are consumed, and 32 cubic inches of carbonic acid formed, or, stating the former at 100, the latter is equal to 84.5. The absolute quantities are here somewhat greater than in Mr Davy's experiments, which might easily happen from the different volume of the lungs, the rapidity of the circulation, or state of the system *; but the relative proportions agree precisely, or at least within two or three fractional parts, with those both of Davy and Goodwyn; and it may be deserving of remark, that these three series of experiments which thus exactly correspond, are those made on natural respiration; while the others, all made in a different manner, present very discordant results.

Excluding, therefore, the experiments of Crawford and Lavoisier, which are exceptionable, as being made by confining an animal in the air breathed,—the experiments of

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peared to me to be from $\frac{1}{40}$ to $\frac{1}{50}$, hence, in the calculation in the text, I took the mean number of $\frac{1}{50}$.

* The absolute quantity of oxygen consumed, is nearly the same with that given by Dr Menzies: he states it at 36 cubic inches in a minute †.

† Dissertatio Inauguralis de Respiratione. Edin. 1790.

Priestley, which are equally objectionable, from the same air having been repeatedly breathed,—and the latter experiments of Lavoisier and Seguin, the results of which are so discordant with each other, as to give reason to doubt of the accuracy of the account that has been given of them; it follows, from the experiments of Goodwyn, Davy, and those which I have stated, all of which were made on natural respiration, that the proportion of oxygen consumed in that procees, is to that of carbonic acid formed, by measure, nearly in the ratio of 100 to 84; and that, therefore, more oxygen is consumed than is necessary to the formation of the carbonic acid expired.

The absolute quantities are not very easily determined with accuracy, as they must vary in different individuals, and in different states of the system; and hence the different results on this point, which may be collected from the preceding statements. From 30 to 38 cubic inches of oxygen are consumed in a minute, and from 20 to 30 cubic inches of carbonic acid formed.

The air expired from the lungs, always contains a portion of watery vapour, as is evident from its condensation when we breathe in a cold atmosphere. The quantity it is difficult to estimate with perfect accuracy. Dr Menzies breathed into a large allantoid, which had been weighed in a delicate balance; the air was allowed to remain in it for some time, to allow of the condensation of the watery vapour, and from the weight the allantoid gained, he concluded, that 2 grains of watery vapour are expired in a minute. Mr Abernethy, by breathing into a glass vessel adapted to condense the water, found the quantity equal to 3 grains in a minute *. In the series of experiments of which I have given an account, I endeavoured to determine the quantity, by putting a quantity of acetate of potassa, a salt extremely deliquescent, into a thin bladder furnished with a stop-cock, and weighing the whole in a delicate balance, then breathing into the bladder for half a minute, and confining the expired air for seven minutes longer. It was then expelled, and the bladder was found to have increased in weight 2 grains. I found, that the acetate of potassa, exposed to the same volume of the air of the room for the same time, increased in weight nearly half a grain; and hence I inferred, what exactly corresponds with Mr Abernethy's estimate, that 3 grains of watery vapour are expired in a minute.

It lastly remains to be determined, what is the influence of the nitrogen of the atmosphere in respiration; and with regard to this different conclusions have been formed. Lavoisier in his early experiments, considered the nitrogen of the atmospheric air as perfectly passive in respiration, and as suffering no change whatever †. Priestley, however, in the experiments already referred to, in which he breathed atmospheric air repeatedly for a certain time, observed an apparent consumption of its nitrogen as well as of its oxygen, 14 ounce measures having disappeared in one experiment in which 100 ounce measures had been thus breathed, and a similar result having been

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* Physiological Essays, p. 141.

† Mémoires de l'Acad. des Sciences, 1777. Mémoires de la Société de Medicine, 1783.

repeatedly obtained. But he adds, " At the suggestion of Dr Blagden, I now think it more probable that the deficiency of phlogisticated air (nitrogen gas) was owing to the greater proportion of it in the lungs after the process than before."

Mr Davy has since, however, investigated this with more care, and has concluded that nitrogen is consumed in respiration. He found in all his experiments, that a quantity of it disappeared; this amounted to about two-tenths of a cubic inch at each natural respiration, 13 cubic inches being the quantity of air taken into the lungs; and as the number of natural inspirations amounted in a minute to 26 or 27, it followed, that in that time 5.2 cubic inches of nitrogen are consumed,—a result which was confirmed by continued respiration, as well as by the respiration of animals confined in a portion of air, though in the latter case the quantity consumed appeared to be less *.

This absorption of nitrogen in respiration appears to be confirmed by some other experiments. It was observed by Dr Henderson, though to a less extent than is stated by Mr Davy, in breathing a portion of air repeatedly from and into the gazometer †; and it appears likewise to be established by the more recent experiments of Pfaff ‡.

These experiments, however, are not altogether free from fallacy, particularly those where the same quantity of air was repeatedly breathed; for, as Mr Ellis has just-

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* Chemical Researches, p. 434.

† Nicholson's Journal, vol. viii. p. 40.

‡ Ibid. vol. xii. p. 249.

ly observed *, the respiration as it proceeds becomes more difficult and laborious, and is at length terminated by a feeble expiration, in consequence of which the due proportion of air is not thrown from the lungs. There appears, therefore, a diminution; and accordingly it is stated by Pfaff, that the diminution and the loss of nitrogen is always greater the longer the air is respired. This indeed does not apply to the experiments performed on natural respiration, at least to the same extent. There remain, therefore, the experiments of Mr Davy performed in this manner, in favour of the consumption of nitrogen; while, on the other hand, it is stated in the account of the last experiments of Lavoisier and Seguin, that " there is neither any disengagement, nor absorption of nitrogen gas during respiration †." It is also to be observed, that from the experiments of Vauquelin, Spallanzani and Ellis ‡, it appears, that there is no sensible consumption of nitrogen by the respiration of the lower orders of animals, while there is the usual consumption of oxygen and formation of carbonic acid.

It appears then, that in respiration oxygen is consumed, and carbonic acid formed; and on an average of the experiments performed in the least exceptionable manner, the consumption of the one is to the production of the other in the ratio nearly of 100 to 84; that therefore more oxygen disappears than exists in the composition of the carbonic acid produced. About 12 or 13

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* Inquiry, &c. p. 114.

† Mémoires de l'Acad. des Sciences, 1789, p. 574.

‡ Inquiry, &c. p. 87, 88.

grains of oxygen are consumed in a minute, and nearly the same quantity by weight of carbonic acid formed. In the same time, 3 grains of watery vapour are expired; and perhaps a small portion of nitrogen is also absorbed. It now remains to take a view of the theories that have been proposed to account for these changes, resulting from the reciprocal action of the blood and the air in respiration, and by which, as has been already remarked, the blood is at the same time converted to the arterial state.

Dr Priestley considered these phenomena as owing to the disengagement of phlogiston from the blood in the lungs, and its combination with the air *, a theory modified and rendered more comprehensive by Crawford. He had originally, in his explanation †, adopted the term phlogiston, and supposed the blood to receive this principle in the extreme vessels, and to give out in the lungs. In the progress of the science, this term required to be defined or expunged; he then substituted hydrogen for it: but as the combination of pure hydrogen with oxygen in the lungs could not account for the production of carbonic acid, he supposed it to be that species of gas which is disengaged from vegetable substances by heat, the heavy inflammable air of the older chemists, the carburetted hydrogen of the modern nomenclature ‡. This hydro-carbon, as it was named, Crawford supposed to be communicated to the blood in the extreme vessels, by which its conversion from the arterial to the venous

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* Philosophical Transactions, 1776.

† Crawford, on Animal Heat, 1779.

‡ Experiments and Observations on Animal Heat, 2d edition.

state was occasioned; in the lungs he supposed it to be given out, and in its nascent state, or its transition to the elastic form, it combined, he supposed, with the oxygen of the air, and formed the carbonic acid gas and watery vapour expired, while the blood deprived of its hydrocarbon returned to the arterial state. The same explanation nearly was given by Lavoisier, at least he supposed the carbonic acid gas and watery vapour of the expired air to be formed by the combination of carbon and hydrogen from the bloodwith oxygen in the lungs.

Lavoisier had also suggested, that the combination of oxygen with carbon might take place in the course of the circulation *; that the oxygen which disappears in respiration may be directly absorbed by the blood, while, on the other hand, carbonic acid might be given out fully formed. This hypothesis was afterwards adopted, and endeavoured to be established by Hassenfratz and La Grange †. They observe, that venous blood exposed to oxygen acquires a vivid red colour, which soon changes to a purple hue; and that arterial blood placed *in vacuo*, or in contact with any gas which does not contain oxygen, quickly assumes the dark purple colour. They conclude, therefore, that the florid red colour of the blood is the result of the absorption of oxygen, while the dark venous colour arises from the intimate combination of that oxygen with a portion of the carbon and hydrogen which the blood contains. According to this theory, then, oxygen is absorbed by the blood in the lungs, remains in the ar-

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[*] Mémoires de l'Acad. des Sciences, 1777, p. 191.

[†] Annales de Chimie, tom. ix. p. 261.

terial blood for a time in a state of solution or loose combination, but it gradually passes, especially in the extreme vessels, into more intimate combination with carbon, forming carbonic acid, in consequence of which the blood passes to the venous state; and from this venous blood the carbonic acid is disengaged in the lungs, and a new portion of oxygen absorbed.

These two hypotheses divided the opinions of physiologists, one or other of them being generally embraced. They are both, however, defective; their principles are far from being proved, and they involve suppositions incompatible with the laws which appear to regulate the chemical actions that proceed in the animal system. No proof is given, in the system of Crawford, of hydro-carbon being communicated to the blood in the extreme vessels; nor is it easy to imagine any source whence this principle in an insulated state could be derived; for, although it has been imagined, both by Crawford and Hassenfratz, that it may have its origin in the solid parts of the system being absorbed, this is at once refuted by the considerations, that this absorption is performed, not by the veins, but by the lymphatics; that it is not sufficiently uniform, nor limited to carbon and hydrogen; that to whatever extent it may be carried, the blood must, in a state of health, deposite as much as is removed; and that there is no evident cause by which the carbon and hydrogen can be separated from the other elements, and be brought into binary combination. And, in the theory of Hassenfratz, though it should be granted, what some facts appear to render probable, that a portion of oxygen is absorbed by arterial blood, there is no proof that this is combined merely with carbon, and that carbonic acid, the result of this combination, is contained in venous blood. We have even proof that the latter supposition cannot be just; for, when arterial blood is exposed to carbonic acid gas until its colour is darkened, it does not recover its florid hue from a subsequent exposure to oxygen [*], and is therefore not venous blood.

Neither are the changes which these hypotheses suppose, at all analogous to the usual chemical changes which take place in the animal system, or sufficiently connected with the purposes which the blood serves in its circulation. They both suppose, that the changes which the blood undergoes, depends not on changes in its composition, strictly speaking, but on the alternate communication and abstraction of a principle held by it in a state of solution, and which appears to serve no purpose in the animal economy, but is assumed merely to account for the phenomena of respiration. The supposition itself is extremely improbable. When the general facility of combination in the principles of animal matter, and the tendency which the actions of the vessels have to form them into ternary or quaternary principles, are considered, it can scarcely be admitted, according to the one theory, that oxygen should be absorbed by the blood in the lungs, without immediately altering its composition; that without being attracted by any of the other principles of the blood, or influenced by the other chemical changes going on in the system, it should be merely combined with carbon, or with carbon and hydrogen, in the proportions necessary to form carbonic acid and water; and that this carbonic acid, without affecting the ultimate composition of the blood, should be carried the whole length of the venous circulation, and thrown out at the lungs. It is equally improbable, according to the hypothesis of Crawford, that carbon and hydrogen should be brought into a state of binary combination in the extreme vessels, and should be held merely dissolved by the venous blood, until acted on by the oxygen of the air in respiration.

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[*] Priestley, Experiments on Air, vol. iii. p. 363. 365.

Still less are the changes which these explanations suppose, connected with the known changes which the blood suffers; for no relation is traced between the process of assimilation or of secretion, and the supposed communication of hydro-carbon, or the combination of hydrocarbon and oxygen, in the extreme vessels.

In any theory of respiration, the conversion of arterial into venous blood ought to be considered as intimately connected with, or rather as the result of the changes which are constantly carried on in the extreme vessels; and this conversion, as well as that of venous into arterial blood, must be regarded as arising from changes in the ultimate composition of the known proximate principles of the blood, and not merely from the alternate communication and abstraction of a principle which it holds dissolved in it, or in what is termed a state of loose combination. According to this view of the subject, the following may perhaps be considered as an explanation of these phenomena.

The blood is the source whence all the parts of the body and the products of the system are formed. Its expenditure is constantly supplied by the chyle, a fluid less completely animalized than the blood itself. The peculiar character of animal matter, with regard to composition, is a large proportion of nitrogen, and a diminished proportion of carbon. It may therefore be inferred, that in the extreme vessels, where the animal solids and fluids are formed, the general process will be the separation from the blood of those elements of which animal matter is composed; and that, of course, carbon, which enters more sparingly into its composition, will exist in the remaining blood in an increased proportion. This is accordingly the general nature of *the conversion of arterial into venous blood.* Nitrogen, hydrogen, and other elements, are spent in the formation of new products, and the proximate principles of the blood, probably the crassamentum chiefly, remain with an increased proportion of carbon. In this state it is exposed, under a very extensive surface, to the atmospheric air in the lungs, the oxygen of which abstracts its excess of carbon, and forms the carbonic acid expired. At the same time another change probably takes place, to serve a different important purpose. A supply of oxygen seems to be required to support the necessary actions of the system; a quantity of it therefore is absorbed by the blood in the lungs, and expended in the extreme vessels. The combination of these changes,—of the abstraction of carbon by the attraction exerted to it by the oxygen of the inspired air, and the absorption of another portion of oxygen, with perhaps even a small quantity of nitrogen, constitute *the conversion of venous into arterial blood.*

There appears little reason to suppose, that any combination of the oxygen of the air with the hydrogen of the blood takes place. The supposition that it does, and that this is the source of the watery vapour expired, originated in the hypothesis of Crawford, which supposed hydro-carbon to be disengaged from venous blood. No fact has ever been stated in its support; it is a combination which can apparently serve no purpose in the animal economy; for hydrogen exists in as large a proportion, (and even in a larger), in animal as in vegetable matter. And there can be no doubt, that the degree of evaporation from a moist surface, so extensive as that of the internal surface of the lungs, at the temperature of 96°, is adequate to account for the whole of the watery vapour expired.

We thus consider the conversion of arterial into venous blood, as intimately connected with, or rather as the result of the other chemical changes going on in the system; and we perceive from this view, the final purpose of the process of respiration. In the extreme vessels, the different constituent principles of the blood are expended in the nourishment of the solid fibre; in the formation of the secreted fluids; and in the support perhaps of the living powers. Of these principles, carbon is that contained in the smallest proportion, in these solids and fluids; it is, therefore, that of which there is the least expenditure, and consequently it must be present in a larger proportion in the blood, after it has undergone these changes. It is evident, that to preserve the due proportion, and prevent it from accumulating, it must be discharged by some other process. Hence the necessity of the application of oxygen to the blood in the lungs, and the origin of the carbonic acid which is uniformly discharged.

We thus too, trace the process of animalization from its first step,—the reception of the aliment to its completion. All animals live directly or indirectly on vegetable matter. The principal difference in the composition of vegetable from that of animal substances is, in the former containing a larger proportion of carbon. Respiration is the function by which this difference is established. The aliment received into the stomach, is soon formed into a fluid capable of assimilating with the blood. It is thus conveyed to the lungs, and loses part of its carbon, or is partially animalized. It is then distributed through the system, and, in the extreme vessels, along with some carbon, parts with so much hydrogen, oxygen, nitrogen, and other elements, as still to leave the carbon predominant. By these reciprocal changes, the conversion of vegetable into animal matter is effected.

It might be supposed, that in any view such as that which has been now given, there must be some difficulty in conceiving that oxygen gas should combine with carbon with so much facility, at a temperature so much lower than that which is in general necessary for their union, and this, too, with the intervention of the coats of the vessels through which the blood circulates,—a difficulty supposed to be obviated in the system of Crawford and Lavoisier, by the carbon being combined with hydrogen, forming an elastic compound, with which, in its nascent state, or in the moment of its disengagement from the blood, the oxygen combined; and in the hypothesis of Lagrange, by the combination between the oxygen and carbon being gradually formed in the course of the circulation. On attending, however, to the objection, it will be found to have no real force. Although carbon, in its solid and insulated form, requires to be raised to a high temperature to cause it to combine with oxygen, yet when it makes part of a ternary or quaternary combination, in which state its cohesion no longer opposes the combination, it is abstracted, and combined with oxygen at any natural temperature. It is thus that many of the vegetable and animal substances, when humid, are altered by exposure to the air, and, as has been already often remarked, carbonic acid formed. Blood itself is acted upon in this manner. It suffers a change precisely similar to that which it undergoes in the lungs, and this more or less rapidly, and to a greater or less extent, according to the quantity of oxygen present, and the degree of agitation used. Arterial blood was exposed by Fontana to atmospheric air for three minutes, when no perceptible alteration was occasioned in the purity of the air: they were then agitated together for three minutes: the volume of air was diminished, and its purity impaired. When oxygen gas was substituted for atmospheric air, the alteration was still more considerable, its purity being diminished even when agitation was avoided; and when it was used, the diminution in purity and volume was still greater. In all these experiments, carbonic acid was also produced *. They therefore prove, that oxygen can attract carbon from

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* Opuscules Physiques, p. 334, 335.

arterial blood. With venous blood, the formation of carbonic acid is still greater, as Luzuriaga ascertained[*], and as has since been established by different chemists. If therefore oxygen can abstract carbon from the principles of the blood, under such circumstances, it is evident it must do so still more rapidly during respiration, where the circumstances are so much more favourable, where there is comparatively a high and uniform temperature kept up, where the blood is exposed on an extensive surface, and in a state of extreme division, and where that surface, as well as the air itself, are rapidly renewed.

Nor can it be supposed, that the thin membrane which forms the coats of the vessels through which the blood circulates can oppose an obstacle to this reciprocal action; for it is known, that animal membrane much more dense than this, is sufficiently pervious to gaseous fluids, and, what is perfectly in point in the present case, that through such membranes, when humid, oxygen can act on blood, and communicate to it the florid colour, precisely as when the blood is freely exposed to it. Thus, Dr Priestley found by experiment, that if a quantity of black blood were inclosed in a moistened bladder, which was tied very close, on hanging it in a free exposure to the air, it acquired "a coating of a florid colour, as thick as it would have acquired if it had been immediately exposed to the open air; so that this membrane had been no impediment to the action of the air upon the blood." Mr Hunter mentions a similar experiment: "I covered," says he, "the mouths of vessels filled with venal blood with gold-beaters' skin, touching the surface of the blood, and the blood constantly became of a florid red on the surface, and even for some depth [*]." It follows, from these facts, that there is no necessity for supposing any organic structure by which these changes may be effected, or any process by which the carbon requires to be separated from the blood and discharged; that fluid may be considered, when circulating in vessels so fine, as exposed to the action of oxygen nearly as if no membrane were interposed: a part of that oxygen approximated to the blood will combine with a portion of its carbon, and the carbonic acid, the moment it is formed, will, from its elasticity, recede and be discharged. The whole action is purely chemical, and precisely the same as that which is exerted between air and blood out of the body, favoured only by the circumstances of exposure, temperature, and agitation, under which it takes place.

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[*] Dissertatio Inauguralis, p. 53, 54.

It is to be stated as an important fact, independent of all theory, that the changes which take place in respiration are much influenced by causes, which occasion an expenditure of certain principles in the extreme vessels. Thus, Dr Crawford established by experiment, that less oxygen is consumed by respiration at a high than at a low temperature [†]; and more lately, this was confirmed in the experiments of Lavoisier and Seguin [‡]; a man consuming, at the temperature of 54°, 1344 cubic inches of oxygen in an hour, while, in an atmosphere at the temperature of 79°, he consumed only 1210 cubic inches. Dr Crawford observed also, that, in an animal placed in a warm medium, the venous blood approached to the arterial in colour; hence it appears, that the high temperature counteracts those chemical changes which the blood undergoes in the extreme vessels, and that the diminution in the consumption of oxygen by respiration is owing to this cause, and not, as has been supposed, to the rarity of the air at the high temperature. If the consumption of oxygen were diminished from the latter cause, the blood ought to be even more completely venous than usual. In the series of experiments by Lavoisier and Seguin, was also confirmed, and shown with perhaps more accuracy, what however had formerly been known, that the consumption of oxygen is influenced by the food and by the state of digestion. They found, that, during digestion, the consumption of oxygen was increased to 1800 or 1900 cubic inches. Exercise, too, considerably increased the proportion consumed. It is stated, that Seguin, in continuing the exercise of raising a weight of 15 lbs. to a height of 613 feet during a quarter of an hour, consumed 800 cubic inches, which is at the rate of 3200 in an hour. And the same exercise made during digestion occasioned a consumption equal to 4600. It is somewhat singular, that the greater or less proportion of oxygen in the air breathed appears to have little influence on the quantity consumed. Lavoisier and Seguin found, that whether an animal breathed pure oxygen gas, or a mixture of it with nitrogen gas in various proportions, the quantity consumed was always the same *. Lavoisier had even observed, in some of his earlier experiments, that less oxygen is consumed when it is breathed pure; and this was afterwards more fully established by Mr Davy, the consumption, according to his experiments, being only 28 cubic inches in a minute, when, in atmospheric air, it amounted to 31. This is accompanied, too, with a diminution in the formation of carbonic acid; the quantity formed, when oxygen was breathed, amounting only to 11 cubic inches, while, from breathing in atmospheric air, it amounted to 26 †. The diminution here is even greater than the proportion in the diminution of the consumption of oxygen; and hence it would appear, that in breathing oxygen gas, though less of it is spent in combining with carbon, more must be absorbed by the mass of blood. These facts are singular, and not easily explained.

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[*] Treatise on the Blood, p. 62.

[†] Experiments on Animal Heat, p. 307.

[‡] Mémoires de l'Acad. des Sciences, 1789, p. 575.

The phenomena of respiration, as now described, are nearly the same in all animals: they all require oxygen, and expire carbonic acid; but the quantities of these are very various in the different orders. In warm-blooded animals, the changes proceed to the greatest extent, and the presence of oxygen is most indispensable; and among these, this also holds in a great measure in proportion to the size of their lungs. In the *amphibia*, the supply of air is less indispensable, as they can sustain the deprivation of it longer, though they still require it, and produce in it the usual changes. Fishes die in water deprived of air, and, according to Dr Priestley, they deteriorate the air contained in the water in which they live*. And the experiments of Vauquelin †, as well as the extensive researches of Spallanzani ‡, have demonstrated, what had before been more or less accurately observed, that insects and worms consume oxygen, and form carbonic acid, though life in these animals is so languid, and remains so long under the suspension of its usual functions, that they can sustain the deprivation of oxygen for a much longer time than animals of the other classes.

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* Mémoires de l'Acad. des Sciences, 1789, p. 575.

† Researches, p. 442.

Connected with respiration, and with the changes which the blood suffers in that process, is the production of animal heat; this arising from changes of capacity which accompany the conversion of arterial into venous, and of venous into arterial blood.

In all the more perfect animals, the temperature of the body is uniformly superior to that of the surrounding medium. Thus, in man it is about 96°; and it remains at that, though we may be exposed to a temperature 40, 50, or 100 degrees below this. It is evident, therefore, that there exists in the system some process causing a constant evolution of caloric, by which this equable and comparatively high temperature is preserved. The action of the air in respiration is demonstrated to be the source of this evolution; and the view which has been given of this subject is undoubtedly the most perfect application of chemistry to physiology, and affords even the most perfect elucidation which we yet have of any function of the living system.

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* Experiments on Air, vol. iii. p. 382.

† Annales de Chimie, tom. xii.

‡ Memoirs on Respiration.

Mayow ascribed the production of animal heat to the action of the air in the lungs; but his opinion, supported by no very decisive evidence, was little regarded. Dr Black, from observing the strict analogy between combustion and respiration, particularly, that in both processes the air undergoes a similar change; and farther, observing that in different animals the superiority of the temperature of their bodies over that of the surrounding medium, is greater the larger their lungs are, and the more air they consume; that in birds, for instance, it is much higher than in quadrupeds, and in quadrupeds than in aquatic animals;—from these observations drew the conclusion, that respiration is the source of animal heat.

It is to Dr Crawford, however, that we are indebted for the full elucidation of this subject, or rather for the theory by which these phenomena are explained, and which he has demonstrated by very extensive and laborious investigations.

From the changes which take place during respiration in the air in the lungs, Dr Crawford proves, that a large quantity of caloric must be rendered sensible. Oxygen is consumed, and carbonic acid formed. But we know, that in the formation of carbonic acid from the combination of oxygen with carbon, a large quantity of caloric must be extricated, since the capacity of the carbonic acid is much inferior to the mean of the capacities of the carbon and of the oxygen gas.

But Dr Crawford at the same time ascertained by experiment, that the capacity of the blood changes when it is converted from arterial to venous, and of course from venous to arterial: the difference between them he found to be as 1.030 to 0.892; that is to say, supposing the capacity of water for caloric to be 1000, the capacity of arterial blood will be rather larger, or 1.030, while that of venous blood will be considerably less, or only 892.

On these facts, Dr Crawford founds his doctrine of animal heat. In respiration, a quantity of oxygen is combined with carbon, so as to form carbonic acid. A quantity of caloric must be extricated in consequence of this combination. But the blood is at the very same time changed from venous to arterial, and by this change acquires an increased capacity for caloric. It therefore takes up the caloric which has been extricated by the combination, so that any rise of temperature in the lungs which would be incompatible with life is prevented. The arterial blood is immediately carried, in the course of the circulation, to the extreme vessels, when it passes to the venous state. In this conversion, its capacity for caloric is diminished as much as it had been before increased in the lungs: the caloric, therefore, which it had taken up is again given out; and this slow and constant evolution of caloric in the extreme vessels over the whole body is the source of its uniform temperature.

It is this view of the changes of capacity which the blood suffers, which forms the peculiar feature and the excellence of Crawford's theory. It might easily have been said, that respiration is the source of animal heat; and the observation of a few analogies, such as those stated by Dr Black, might have given probability to the assertion. But it must always have been difficult to conceive how this heat, if derived from this source, was not rendered sensible in the lungs, or how it was equally distributed over the body. This is fully explained from the changes of capacity which the blood suffers in its conversion from the venous to the arterial, or from the arterial to the venous state,—changes not hypothetically assumed to explain the phenomena, but established by experiment. Yet it is singular how much this has been misunderstood, and how often the objection in the following passage, which I quote from a modern systematic writer, has been urged by physiologists: "Si la chaleur vital tirait sa source unique des poumons, elle devrait être dans ces organes incomparablement plus forte qu'elle ne l'est par tout ailleurs; et l'activité de cet embrasement, necessaire pour echauffer tout le corps, irait à detruire la substance des parties qui en seraient le foyer *." The same objection has even been urged by Lagrange and Hassenfratz †, who ought to have known better the doctrine of specific heat.

This admirable theory has been confirmed by other experiments, and independent of the direct facts upon which it has been founded. Dr Crawford himself, and afterwards Lavoisier and La Place, found, that when an animal is confined in a vessel contrived so as to measure the quantity of caloric which it gives to the surrounding medium in a certain time, and the quantity of oxygen consumed by the animal in that time, this quantity of caloric corresponds nearly to the quantity evolved from the combustion

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* Dumas, Principes de Physiologie, tom. iii. p. 555.

† Annales de Chimie, tom. ix. p. 266.

of carbonaceous matter, such as wax or oil, in the same quantity of oxygen. It has been found, too, that whatever increases the heat of the body, such as violent exercise, or, in general, whatever augments the circulation, increases the consumption of oxygen in the lungs.

I may add, that this explanation of the production of animal temperature is altogether independent on any particular theory of respiration. Whatever may be the nature of the difference between venous and arterial blood, whether the latter contain oxygen or not, or whether the former hold in solution hydro-carbon, carbonic acid, or any other principle, it is proved by experiment, that the blood in these two states has different capacities for caloric; and on this fact the explanation of the origin of animal temperature depends. It is equally unimportant, whether the combination of oxygen with carbon be supposed to take place in the lungs or in the course of the circulation; since from this combination the carbonic acid expired is derived; and therefore, wherever it takes place, it must be attended with an evolution of caloric. The explanation according to both opinions is ultimately the same, and the merit of the theory remains with Crawford.

When an animal is placed in a medium, the temperature of which is considerably high, it still preserves its temperature nearly uniform; the animal heat not rising much above the natural standard, as has been fully demonstrated by the experiments of Tillet * and of For-

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* Mémoires de l'Acad. des Sciences, tom. xxxiii. p. 322.

dyce and Blagden *. In this case, it has been ascertained by the experiments of Crawford, that the usual change of arterial into venous blood does not go on, the blood in the veins being nearly as florid as in the arteries. It is evident, therefore, that no evolution of caloric will take place; and it is even possible, that the temperature of the body may be kept low by the blood acquiring an increased capacity for caloric, though other circumstances, particularly the imperfect conducting power of the animal solids, and the increased perspiration, have a share in the effect.

TRANSPIRATION is a function very analogous to respiration, and ultimately producing, perhaps, the same changes in the blood. Carbonic acid gas is exhaled from the skin as from the lungs, and oxygen absorbed. There is also an exhalation of aqueous vapour, which, when augmented by heat or exercise, is condensed on the surface, and forms the sweat. Count de Milly observed, that when the hand was kept for some time in warm water, a quantity of air was disengaged from the surface, which was found to be carbonic acid. The same fact was established by the experiments of Cruickshank †. And Abernethy and Jurine further proved, that there is a consumption of oxygen. The former chemist exposed his hand to seven ounce measures of atmospheric air, confined over mercury for five hours; at the end of that time the air had diminished in volume half an ounce mea-

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* Philosophical Transactions, 1775.

† Cruickshank on Insensible Perspiration.

sure, and by agitation with lime-water, one ounce more was absorbed, the lime-water being rendered milky; the residual air contained one-sixth less oxygen than before the experiment. When the hand was exposed to the air for nine hours, the quantity of carbonic acid gas produced, amounted to rather more than an ounce measure, and the residual air contained one-fourth less oxygen than before *. Jurine found, that on fixing bottles containing atmospheric air, to the surface of the skin, the air was vitiated, diminished in volume, and contained carbonic acid †. These changes in the air are also accompanied, as in respiration, with the exhalation of watery vapour. Mr Cruickshank, by inclosing his hand in a glass vessel, the orifice of which was secured by being tied over at the wrist with bladder, observed that the glass soon became dim, and drops of water were condensed on its surface. In this way about 30 grains of water were collected in an hour, though on repeating the experiment the quantity was sometimes much less, and at other times, especially after exercise, was greater ‡. It is known also to be much augmented by heat. From these facts it is apparent, that the skin performs functions, with regard to the atmosphere, the same as those performed by the lungs; and they are no doubt connected with the same changes in the blood: though it appears, that the effects produced by the air on the blood, through the medium of the skin,

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[*] Physiological Essays, p. 118.

[†] Mémoires de la Société de Medicine, tom. x.

[‡] Experiments on Insensible Perspiration, p. 69, &c.

are much less considerable, owing no doubt to the density of that membrane.

Lavoisier and Seguin, in their researches, endeavoured to determine what proportion the changes by transpiration bear to those by respiration *. They employed a covering of silk rendered air-tight by being coated with a varnish of caoutchouc, and adapted to the body, so that the products by the skin could be separated from those by the lungs. By taking the weight, before entering the apparatus and after leaving it, the whole loss of weight in a given period could be ascertained; and by weighing a few moments after being inclosed in the apparatus, and a few moments before withdrawing from it, the loss of weight from respiration alone was determined, and thus the proportion by each process could be established. The following are the results: The loss of weight sustained by an individual, not under any unusual bodily labour, varies from 11 grains in a minute to 32, or in twenty-four hours from 1 lb. 11 ounces 4 drachms, to 5 lbs; this including the effects from transpiration and respiration. The mean loss is 18 grains each minute, 1 ounce 7 drachms an hour, or 2 lbs. 13 ounces in twenty-four hours: and in separating the effects of each of these functions, of these 2 lbs. 13 ounces, there belong to cutaneous transpiration 1 lb. 14 ounces, and to respiration 15 ounces. These results can, however, be regarded only as approximations: the uncertainty of those which relate to respiration have been already noticed; and with regard to the general effects from transpiration, it appears from the

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* Mémoires de l'Acad. des Sciences, 1790, p. 601.

account given by Seguin, that the watery product only had been attended to, and that there had been no estimate of the oxygen consumed, or carbonic acid exhaled by the skin.

The skin appears to secrete a small portion of acid, as it sometimes is capable of communicating to the more delicate vegetable colours a red tinge, and distilled water rubbed on it is rendered turbid by nitrate of silver. Some chemists have supposed this to be the muriatic, others the phosphoric acid. In a state of disease, it is probable that the products by this organ are still more diversified.

SECT. II.

OF THE CHYLE.

THE food digested in the stomach, passes into the intestinal canal; and in its progress, there is separated from it by the absorbents which terminate on the internal surface of the intestines, a white milky liquor, which is conveyed by these to the thoracic duct, and ultimately into the blood. This is the Chyle,—a fluid, the composition of which is important, as it is from it the blood is formed, and by its medium nutrition conveyed, but which, from the difficulty of procuring it, has not been examined with that attention its importance demands.

Its colour is white, its taste is sweet, and, as has been said, somewhat saline. On standing, it is affirmed, that a cream forms on its surface, and also that it coagulates, Hallé found, that after it had been exposed to the air for a short time, it assumed a gelatinous form, and presented a kind of firm coagulum, adhering to the sides of the vessel. Under this was a portion of liquid, thin, and of the colour of milk. The coagulated mass is semi-transparent, and has a light red tinge *. According to Fordyce, besides this matter which coagulates spontaneously, the chyle contains a fluid that coagulates by heat †.

Very discordant results have been obtained from experiments made on the effect of substances introduced into the stomach, on the composition and properties of the chyle. Colouring matter mixed with the food, appears sometimes to communicate to it a tinge, sometimes not. According to Lister, it receives a blue colour from indigo received into the stomach; an observation confirmed by Haller, who did not find, however, any effect from other substances, which had likewise been said to give it colour. Dr Fordyce also observes, that indigo thrown into the intestines renders the chyle quite blue, and that musk communicates to it a strong odour. This intermixture of substances, however, conveyed by the stomach, does not always happen. It has been found, that when iron is mixed with the food, no traces of it are to be discovered, by the test of infusion of galls in the chyle ‡; and this has been stated as an argument to prove, that iron is not derived from without, but is actually formed in the animal system.

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* Fourcroy's System, vol. x. p. 91.

† Treatise on Digestion, p. 121.

‡ Ibid, p. 122.

SECT. III.

OF MILK. SUGAR OF MILK. SACCHO-LACTIC ACID.

Milk is the fluid designed for the nourishment of young animals, and secreted by a particular glandular apparatus in the mammæ of the female. It differs somewhat in its sensible qualities in different animals, but its chemical properties appear to be nearly the same. These have been often the subject of investigation; which has been so far successful, that the proximate principles of this fluid are now known, though we are still unable to trace the changes by which it is converted into blood. Besides the knowledge of it, which we have received from the older chemists, an elaborate examination of it was some years ago undertaken by Parmentier and Deyeux *, and more lately some facts with regard to it have been added by Lagrange †.

Milk is white and opaque, its taste is bland and sweet, its smell faint; its consistence is somewhat thick, and its specific gravity a little greater than that of water. These qualities vary, however, not only in different animals, but likewise according to the diet and state of the digestive organs, and even according to the period, after food has been taken, at which the milk has been formed.

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* Expériences sur le Lait.

† Nicholson's Journal, vol. x. p. 141.

When milk newly drawn is allowed to remain at rest, it suffers a slight spontaneous decomposition, a thick white very bland fluid collects on the surface, and the fluid beneath is more watery. This change has been ascribed by some chemists to the action of the air; but others, particularly Young, have asserted that it takes place equally when the air is excluded,—an observation since confirmed by Thenard. This seems indeed more probable, since, from the whiteness and opacity of milk, it is obvious that an oily fluid is diffused through a watery one, and white globules are even discovered in it by the microscope. It is these, probably, that separate spontaneously when the milk is at rest, and form the cream.

The Cream is a substance of an oily nature, and, when agitated for some time, separates into a fluid and a solid part, the latter having all the properties of a concrete oil. This oily substance, then, or Butter, is the first proximate principle which a simple analysis discovers in the milk. It is bland and sweet, but becomes rancid on exposure to the air. By distillation, it is converted principally into a fluid oil, and, when decomposed by heat, affords the same products as animal fat. The cream, therefore, is merely a mixture of this oily matter with the cheese and whey, which form the other parts of the milk.

When the milk is allowed to stand after the spontaneous separation of the cream, it begins to suffer another change, which is more rapid in a high than low temperature. It first becomes acescent, and then coagulates. When this coagulum is pressed gently, a serous fluid is forced out, and a solid dry matter, somewhat elastic, and insoluble in water remains. This is the caseous part of milk, or the pure Cheese.

This change appears to be owing to the formation of a small quantity of acid in the milk on standing, which re-acting upon it, separates the caseous matter. We accordingly find, that acids added to milk, even though very weak, immediately coagulate it: many other substances have the same effect, as several neutral salts, especially those containing an excess of acid, alkohol, sugar, gum, the gastric juice of animals, and the juices of several vegetables. This caseous matter is also separated by mere heat. If milk be moderately heated in contact with the air, a thin pellicle forms upon its surface: if this is removed, or allowed to fall to the bottom of the vessel, a new one is formed, and this continues for a considerable time. After the formation of them has ceased, the remaining fluid is thin and serous. Parmentier and Deyeux have ascertained, that these pellicles consist of a matter perfectly identical with the cheese. The separation of it from the milk is promoted by the contact of the air, but apparently merely by its mechanical action, and not by any chemical effect; since its separation, they found, was equally promoted by oxygen, hydrogen, or carbonic acid gas.

The coagulum separated by these different substances is nearly the same in its properties. The liquor, however, found in the stomach of young animals, or what is termed Rennet, is preferable in order to obtain its full separation. The curd that is formed by adding it to milk moderately heated, is merely the caseous matter retaining a portion of the serum or whey, which can be easily separated by pressure. The coagulating power of the rennet was ascribed to a portion of acid which it contained; but Young, and more lately Parmentier and Deyeux have shown, that it is the property of the juice itself, since, even when an alkali is added to it, so as to be in excess, it retains the coagulating power. The membrane of which the stomach is composed likewise possesses this property, and communicates it to water macerated upon it. The cause of the coagulation is not well understood.

The Caseous matter of milk is a white or greyish substance, somewhat elastic: when fresh, it is nearly insipid; but becomes acrid on keeping. It is insoluble in cold water, but by boiling its texture is destroyed.

If left exposed in a moist state to the air, it very soon putrefies. If the moisture has been pressed out of it, and especially if it has been dried by a gentle heat, it remains a long time unchanged.

The pure fixed alkalis, dissolved in water, and assisted by a moderate heat, act upon the caseous matter readily. It is dissolved, and at the same time ammonia is exhaled, probably formed by the combination of its elements. If an acid is added to the solution, a precipitate of a dark red colour is thrown down, and a smell of sulphuretted hydrogen is perceived. Silver is also blackened by the liquor in a short time. Ammonia is likewise capable of dissolving the caseous matter.

The mineral acids, when diluted with water, effect a solution of it, but not completely. The vegetable acids, particularly vinegar, dissolve it entirely, and with more facility. Nitric acid disengages from it nitrogen gas.

The caseous matter decomposed by heat affords an empyreumatic oil, ammonia, and a species of carburetted hydrogen. A residuum of charcoal is obtained, which, when burnt, affords a small quantity of fixed alkali, and also, as Scheele ascertained, and Lagrange has confirmed, a portion of phosphate of lime.

The caseous matter must be admitted as a principle differing in some respects from any other animal matter. It seems most analogous to the albumen, as it is soluble in a fluid resembling the serum of the blood, and as it is coagulated by heat. In several other of its properties, it is analogous to fibrin, and is probably intermediate between these. It is the most animalized product of the milk, and is undoubtedly that which is most nutritious.

The distinction must be noticed between this pure cheesy matter and that which is formed from the milk before the cream is separated. This latter kind of cheese is the caseous matter mixed with the butter; and in the different kinds of cheese that are prepared for use, the qualities depend principally on the proportion of these to each other.

When these two principles, the butter and the cheese, have been separated from the milk, there remains a liquor named the Serum or Whey. The composition of this is lastly to be noticed.

The whey has a yellowish colour and very slight tenacity: its taste is bland and agreeable. It still contains a portion of caseous matter, which is separated by allowing it to stand in a warm place for some hours: it then becomes acescent, the cheese separates in filaments, and, by filtration, the whey becomes transparent.

When this pure whey is subjected to evaporation, it affords a substance of a granulated saline appearance, of a sweet taste and a yellowish colour, which, by solution and filtration, yields, on evaporation, a salt of a white colour, in rhomboidal crystals. This substance, which is the principal solid matter in the whey, is named the Salt or Sugar of Milk. In some countries, particularly in Switzerland, it is prepared in considerable quantity.

This substance is soluble in seven parts of cold and four of boiling water. It is decomposed by heat, and affords products nearly the same as those yielded by vegetable saccharine matter.

When the sugar of milk is treated with nitric acid, assisted by a moderate heat, nitrous gas is discharged, the solution becomes yellow, and, as it advances, a copious deposition of a white matter takes place. The fluid, when poured off, affords by evaporation crystals of oxalic acid.

The white matter obtained in this operation is possessed of the properties of an acid. Scheele, who discovered it, supposed it to be one of a peculiar kind, and gave it the name of Acid of Sugar of Milk. In the new nomenclature, it is named the Saccho-lactic Acid.

Scheele concluded, that this substance is not formed in the above process, but that the sugar of milk is a compound of it and saccharine matter, and that it is merely rendered sensible by the saccharine matter being oxidized by the nitric acid. Parmentier and Deyeux accede to this opinion. They observe, that in the process in which it is obtained, very little of the nitrous acid is decomposed, and that, if the quantity actually decomposed be compared with the quantity of oxalic acid formed, the proportions will be found nearly the same as when the oxalic acid is procured by the direct oxygenation of pure sugar. And they add the synthetical proof, that when two parts of the saccho-lactic acid are mixed with one of sugar, a compound very similar to the sugar of milk is formed. The opinion, however, as is justly observed by Fourcroy, appears to accord very ill with what we know of the properties of these two substances.

Saccho-lactic acid is obtained by the process already described, in the form of a white powder, a little granulated: its taste is slightly sour: it is sparingly soluble in water, 60 parts even of boiling water being requisite, according to Scheele, to dissolve it: this solution has an acid taste, and reddens the vegetable colours: it deposites, on cooling, small crystals. At the temperature of 212°, it decomposes the alkaline carbonates, disengaging the carbonic acid. Exposed to heat in close vessels, it is decomposed, the products being an acid liquor, which, on standing, deposites needle-like crystals, an empyreumatic dark-coloured oil, carbonic acid and carburetted hydrogen gases, and a large residuum of charcoal.

This acid combines with the different salifiable bases, forming salts named Saccholates; but we have no knowledge of these combinations, except from a few observations by Scheele. It forms with potassa a salt soluble in eight parts of warm water, which crystallizes on cooling; and with soda a salt equally crystallizable, and rather more soluble, requiring only five parts for its solution. Both these salts are more soluble, from an excess either of the acid or of the base. Saccholate of ammonia is very easily decomposed by heat, the ammonia being expelled. The compounds with lime, barytes, and magnesia, are nearly insoluble; hence this acid decomposes the soluble salts of these earths. It acts feebly on the metals; and with their oxides, so far as has been examined, forms salts of sparing solubility. It thus precipitates the nitrates of silver, quicksilver, and lead.

This acid is formed, not only from sugar of milk, but likewise, as has been already remarked (p. 118.), from gum, by the action of nitric acid: two parts of the acid being slightly heated on one part of gum, until a small quantity of nitric oxide and carbonic acid is disengaged, on cooling, the liquid deposites the saccho-lactic acid; the quantity, according to Fourcroy and Vauquelin, being from 14 to 26 parts from 100 of gum.

From the quantity of saccharine matter which milk contains, the whey is susceptible of both the vinous and acetous fermentation; and by the Tartar tribes, a vinous liquor is actually prepared from mares milk. The process has been described by Dr Guthrie *. The liquor however is extremely weak, eight pints of it affording, on distillation, only four ounces of alkohol.

It passes much more readily into the acetous fermentation, or becomes acescent, from the production of an acid, which it now appears is the acetic. Scheele first examined this acid, and although he observed an analogy to the acetic acid in its properties and combinations, he found also some differences between them. He was unable to obtain it pure by distillation; for although an acid liquor distilled over, this could not be carried far, as a decomposition and a deposition of carbonaceous mat-

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* Edinburgh Philosophical Transactions, vol. ii.

ter took place from the heat applied. He supposed, too, that this acid decomposed the acetates. Hence he regarded it as different from the acetic; and in the new nomenclature it received the name of Lactic Acid. From the recent researches, however, of Lagrange, and of Fourcroy and Vauquelin, it is established that this acid is nothing more than the acetic, disguised by a portion of extractive matter united with it, and by the saline substances contained in the whey *. According to the observation both of Thenard and Lagrange, a portion of free acetic acid is always contained in milk, and is procured from it by distillation.

Besides the sugar of milk, which is the principal ingredient dissolved in the serum, there are present some other saline substances, and which remain dissolved in the liquor after its crystallization. These, according to the observations of Scheele and Vauquelin, are principally muriates of lime, potassa, and soda, with phosphates of lime, magnesia, and iron.

Such, then, is the composition of milk. It consists of an oily substance, of the caseous matter, of the peculiar substance named sugar of milk, and of a small portion of neutral salts dissolved in water. The union of the three first, two of which approximate to the nature of vegetable, and the third to that of animal matter, renders it a fluid at once nutritive and easy of digestion; and, as Vauquelin has remarked, the presence of the phosphoric acid with the lime and iron, fit it well for the formation of blood.

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* Nicholson's Journal, vol. x. p. 264.

SECT. IV.

LYMPH. MUCUS.

The fluid contained in the lymphatic vessels, and passing into them either from the extremities of the arterial branches, or taken up by absorption from the surface of the internal parts of the body, has from its origin been regarded as analogous to the serum of the blood. This, however, is not well established; it is even probable, that though derived from that fluid, it may have undergone some alteration, and its properties therefore require to be noticed. They are however but imperfectly known, principally from the difficulty of procuring it in a pure state.

Lymph is pellucid and insipid: it is also said to be slightly viscid, miscible with cold water, and coagulated by heat, by the acids, and by alkohol. If these properties strictly belong to it, it might be regarded principally as a solution of albumen; but there is some uncertainty whether these observations refer to pure lymph or to the serum of the blood, from these fluids having been assumed to be ultimately the same.

This fluid frequently undergoes, on the surfaces on which it is effused, a degree of inspissation, probably from its watery part being absorbed; and it then forms what has been named Mucus, which covers the passages and internal cavities of the body. This term, it must be acknowledged, is rather vague. Mr Hatchet had regarded it as similar to gelatin, only that when heated, it does not become gelatinous. Dr Bostock has, on the contrary, applied it to denote a peculiar principle of animal matter, existing in what is usually named mucus, as well as in a number of the animal fluids. The following are its properties, as he has assigned them. It may be obtained solid by evaporation, and is again soluble in water. It is insoluble in alkohol or ether. It neither coagulates, nor becomes gelatinous, when its solution is heated; characters by which it is at once distinguished from albumen and gelatin. Neither is it precipitated by tannin, or by corrosive muriate of mercury. The acetate of lead, or Goulard's extract, produce a copious white precipitate with it, and this forms its most certain test. Dr Bostock has remarked its close resemblance in these properties to vegetable gum *.

This principle, when in its liquid state, suffers inspissation from exposure to the air. The mucus of the nostrils, which has been examined by Fourcroy and Vauquelin, appears to be in this state. They observe, that this mucus, as it is first secreted, is liquid and clear, a little viscid, without smell, and of a taste somewhat saline; it becomes thick and viscid from exposure to the air, or to a gentle heat; and the residuum which it at length affords by evaporation, affords crystals of muriate and carbonate of soda, and phosphates of soda and lime. From the carbonate of soda it contains, it renders green paper stained with the juice of the mallow. It also contains an animal matter not albuminous, but which becomes quickly thick and concrete from the action of the

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* Nicholson's Journal, vol. xi. p. 251. vol. xiv. p. 144.

oxygen of the atmosphere, or of oxymuriatic acid, and acquires opacity and a yellowish or greenish colour. It is more or less in this state as it covers the passage of the nostrils, from the action of the air, and is completely inspissated when a person has been exposed to the vapours of oxymuriatic acid. In this inspissated state, water does not dissolve it, nor can it easily be diluted with that fluid either cold or warm. The acids added in small quantity thicken it, but in a larger proportion they redissolve it, giving it different colours. Muriatic acid appears to effect this solution most easily. The alkaline or earthy salts do not dissolve it. It is very little liable to putrefaction, when kept even in a humid state. Like all the other animal fluids it is subject to alterations from morbid affections, which influence its secretion *.

Fourcroy and Vauquelin have farther observed, that the liquid which forms the tears is nearly the same with the nasal mucus. It is clear as water, without smell, having a taste somewhat saline and a specific gravity rather greater than that of distilled water. It renders green paper tinged with juice of violet or mallow, a property which appears to be owing to the presence of soda. When heated it is inspissated, a change which it suffers also quickly from exposure to the air; it becomes viscid, and acquires a yellowish or greenish colour. It also affords cubic crystals, containing an excess of alkali which alkohol dissolves, leaving the mucus part undissolved. In this inspissated state this liquid is also insoluble in water. The alkaline solutions which have no effect on the liquid,

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* Fourcroy's System, vol. ix. p. 432.

as it is first secreted, dissolve it after it has suffered this change, and restore to it its fluidity and transparency. The acids exert no action on it at its first discharge, except saturating the free soda: but when it has been inspissated by exposure to the air, they exhibit with it peculiar phenomena. Sulphuric acid disengages carbonic and muriatic acid gases, by decomposing the muriate and carbonate of soda which it contains. Muriatic and acetic acid produce only a slight effervescence. Oxymuriatic acid causes coagulation, and flocculi are separated, a change apparently produced by the communication of oxygen. Alkohol forms also white flocculi in this liquid. From the experiments of these chemists it follows, that the tears are formed of a large quantity of water, which holds in solution an animal matter not albuminous, as it is not coagulated by the acids, and which appears to have the characters of mucus, with which are associated various saline substances,—muriate of soda, pure soda, phosphate of soda, and phosphate of lime. The last, when it accumulates, forms the concretions sometimes found in the lachrymal glands*.

I have placed the history of these fluids under one section, as they appear to have very strict relations, both physiological and chemical, and are probably ultimately the same, or at least are so with very slight modifications.

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* Fourcroy's System, vol. ix. p. 426.

SECT. V.

SALIVA. PANCREATIC FLUID.

The fluid secreted in the salivary glands is designed to promote the mastication, and perhaps also the farther digestion of the food. Its taste is very slightly saline; it has also a slight degree of viscidity, in consequence of which it is frothy, or retains the air entangled in it. It does not mix very readily with water: by trituration it may be diffused through it; but a portion of matter which Dr Bostock considers as coagulated albumen, remains undissolved. When exposed to the air, a pellicle forms on it; it becomes turbid and deposites flocculi, changes which have been ascribed to oxygenizement; it has been said, indeed, to have an unusual tendency to absorb oxygen; and hence it has been affirmed, that it promotes greatly the oxidizement of the metals; the extinction of mercury by trituration being much facilitated by it, and even gold and silver leaf being oxidized when triturated with it *. This property probably depends on its mucus.

When the liquid formed, by triturating saliva with water, is exposed to heat, it is slightly coagulated, and a flocculent precipitate appears. This denotes the presence of albumen. It is also coagulated or inspissated by alkohol, and by the stronger acids. The fixed alkalis and the earths

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* Fourcroy's System, vol. ix. p. 445.

cause an ammoniacal odour to exhale from it, by decomposing the ammoniacal salts it contains: the alkalis at the same time dissolve it. Lime-water throws down from it a precipitate of phosphate of lime; and oxalic acid detects in it the presence of lime in small quantity. The metallic solutions, especially the nitrates of lead, mercury and silver, render saliva very turbid, and cause an abundant precipitate; partly from their action on the animal matter, and partly by decomposing the phosphates and muriates it contains. Acetate of lead, or Goulard's extract, produces a copious precipitate in saliva diluted with water and rendered clear by filtration, probably from its action on the mucus which exists in it *.

When saliva is evaporated by a gentle heat, cubical crystals of muriate of soda are discoverable in the residuum, as well as crystals similar to those of muriate of ammonia †. When evaporated to dryness it leaves a residuum, which swells and inflames on ignited fuel, exhaling a fœtid odour, with a smell of prussic acid. Its residual charcoal, when it is subjected to destructive distillation, affords considerable quantities of muriate of soda, phosphate of soda, and phosphate of lime.

Saliva appears to be a solution, in a very large quantity of water, of albumen, mucus, and certain saline substances—compounds of phosphoric and muriatic acids, with soda, ammonia, and lime. The proportions are conjectured by Dr Bostock to be about 80 of water, 8 of

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* Bostock, Nicholson's Journal, vol. xiv. p. 247.

† Fordyce on Digestion, p. 52.

coagulated albumen, 11 of mucus, and 1 of the saline compounds.

The concretions which are sometimes deposited in the excretory ducts of the salivary glands, are stated by Fourcroy to consist of phosphate of lime, with animal mucilage; and the incrustation formed on the teeth from the saliva, and known by the name of Tartar of the Teeth, is said to be of a similar nature.

THE similarity of the PANCREATIC JUICE, or liquid secreted by the pancreas, to the saliva, has always been observed by physiologists, but it has undergone little chemical examination. Dr Fordyce, from a small quantity of it which he obtained, found it to be liquid and colourless, having a taste slightly saline. On allowing it to evaporate, crystals were deposited, similar to those from the saliva, and muriatic acid was indicated by the test of nitrate of silver. On evaporation also, a colourless mucus was obtained, which redissolved in water, though the compound with water, to use Dr Fordyce's expression, is not very diffusible through water *. From these facts it appears to be extremely analogous to saliva, and probably, as physiologists have conjectured, serves the same purpose in promoting the digestion of the food.

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* Treatise on Digestion, p. 70.

SECT. VI.

GASTRIC FLUID.

No fluid presents more singular properties, than that which is secreted by the glands of the stomach, and which is of so much importance in the process of digestion. From its connection with that process, its properties have been often the subject of investigation, and a number of facts with regard to it have been discovered by the successive labours of Reaumur, Stevens and Spallanzani.

The principal difficulty in submitting it to experiment is, that of obtaining it pure; for as there is no duct whence it can be collected, it is always liable to be more or less mixed with the contents of the stomach. The method which Spallanzani employed, was to cause an animal to swallow small pieces of sponge, when it had fasted so long as that the food might be supposed to have been evacuated from the stomach, and after some hours withdrawing these bits of sponge, by a string attached to them. By pressing them over a glass capsule, the gastric fluid which they had imbibed was obtained. It may also be collected from the stomach of an animal newly killed, and which had previously been kept some hours without food; but the quantity that can thus be procured is not considerable. In the operation of vomiting it frequently happens, that after the solid contents of the stomach have been discharged, when the vomiting recurs, a colourless fluid, more or less viscid, is brought up, which has been regarded as the gastric juice. Dr Fordyce has remarked, however, that he had often examined this fluid, and found it to be water, with a small quantity of saline matter, and little or no mucilage, and to be destitute of one of the most characteristic properties of the gastric fluid, that of coagulating milk.

The gastric fluid obtained by Spallanzani, was, in all the orders of animals from whom he procured it, whether gramnivorous or carnivorous, similar in appearance and physical qualities. If unmixed with any of the food, it was clear, or its transparency was at least little inferior to that of water. Its taste was always somewhat saline, and frequently also bitter: this bitterness, as well as a tinge of yellow which it sometimes had, being undoubtedly owing, as he supposes, to the presence of bile. Sometimes it was procured without any sensible bitterness, and its taste was then merely saline. He could not discover in it any indication of acidity, except sometimes in animals feeding on vegetables, and the acidity was then evidently to be ascribed to the intermixture of the food, and the changes it had undergone [*]: it was equally free from any alkali. In a further examination of its properties, undertaken at the desire of Spallanzani, by Scopoli, it was found, when triturated with lime, to emit a fœtid odour. It precipitated silver in the state of muriate, from nitrate of silver: evaporated it gave a solid residuum, deliquescent, and having an unpleasant odour. Subjected to destructive distillation, muriate of ammonia was sublimed from it [†].

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[*] Spallanzani's Dissertations, vol. i. p. 327.

[†] Ibid. p. 55. 87. 282. 329.

To this very imperfect account of the qualities of the gastric fluid, some facts have been added by Macquart and Vauquelin. They obtained it from the stomachs of sheep and calves; they always found in it free phosphoric acid and phosphates. A small quantity of albumen was separated from it by the action of acids, besides a portion of mucus or gelatinous matter *.

Spallanzani had observed, that the gastric fluid is little liable to putrefaction. Obtained from his own stomach by vomiting, he remarks, that " it did not change colour or taste, nor did it acquire any bad smell, though kept above a month, in the hottest season of the year;" and he observes, that this is a property common to every gastric fluid he had examined †. Nay, he found, that it prevents substances from putrefying, and even that animal matter, which had become putrid and offensive, was recovered and rendered free from this, by maceration in the gastric fluid, either out of the body or in the stomach of the animal ‡. These properties, however, were not observed by Macquart and Vauquelin in the gastric fluids they examined; on the contrary, they became corrupted in a few days. The observation of Spallanzani is, however, confirmed by the experiments of Stevens.

The most singular property of this fluid, and one which is undoubtedly chemical, is its solvent power with regard to the food,—a power unequivocally established by the multiplied researches of Reaumur, Stevens, and Spallan-

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* Fourcroy's System, vol. x. p. 11.

† Dissertations, vol. i. p. 185. 283.

‡ Ibid. p. 348, &c.

zani. Reaumur inclosed articles of diet in metallic tubes open at both ends, which he forced animals to swallow; employing those substances, with regard to each, on which they naturally feed. By this contrivance he avoided the action of pressure and trituration, which had been considered as the principal causes of digestion, and exposed the food merely to the action of the gastric fluid. He found, that in animals with a membranous stomach, and which usually feed on flesh, the inclosed food was dissolved, more or less completely, according to the time during which the tubes were allowed to remain in the stomach; and he hence inferred, that the gastric fluid of these animals is possessed of a solvent power. He found, however, that in those animals which have a muscular stomach, capable of strong contraction, and therefore of performing the office of trituration, the substances inclosed, (grains chiefly on which these animals feed, though sometimes also grass, or even flesh), were not at all dissolved; and hence he concluded, that in these animals the gastric fluid is not a solvent, and that the digestion of the food is effected by trituration. Spallanzani rectified this conclusion; he shewed, that the trituration is necessary only to bruise the food, and thus prepare it for the action of the gastric fluid, and that when previously bruised, or when from any other preparation it is in a soft or humid state, and inclosed in tubes, it is dissolved by these being allowed to remain in the stomach *. He further found with Reaumur, that in animals with a membranous stomach, the solution of the food inclosed in tubes, takes place very

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* Dissertations, vol. i. p. 35.

readily [*]. And what is still more decisive with regard to the solvent power of the gastric fluid, he found, that the different substances used as food, both flesh, bread, grain, and grass, submitted to its action out of the body, at a temperature not higher than that of animals, were dissolved [†]. It appears from his researches, that in animals with a membranous stomach, the solvent power is greater than in those with a muscular stomach, by the exertion of which the food is bruised; and in some of the former, in the dog, for example, or the eagle, the solvent power is very considerable, the hardest bone inclosed in tubes being speedily dissolved.

With the experiments of Spallanzani those of Stevens in general agree [‡]. Availing himself of a man who had the power of swallowing hard substances without injury, he gave to him almost all the articles of food, vegetable or animal, inclosed separately in hollow spheres of silver, perforated with a number of holes, and found, that when thus introduced into the stomach, they were speedily dissolved. And continuing his experiments on animals, he established nearly the same results as Spallanzani had done. He found too, that the gastric fluid out of the body exerts its solvent power. Half an ounce of the gastric juice of a dog was put into a phial with twelve grains of roasted beef, and the same quantity of the same beef was put into another phial with water. Both were exposed to a temperature of from 102 to 104: in eight hours, the beef in the gastric fluid was completely dissolved, while that in the water was not sensibly altered : in twenty-four hours, the latter was putrid, while the former had merely a pungent odour, probably from a slight scorching from the heat. When the experiment was repeated with flesh masticated, the solution was sooner completed ; and in a similar manner, many other substances, both animal and vegetable, were dissolved.

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[*] Dissertations, vol. i. p. 69, 70. 108. 258.

[†] Ibid. p. 93. 170.

[‡] Dissertatio Inauguralis, Edin. 1777.

In one point, the experiments of these physiologists do not perfectly correspond. Stevens found, that those kinds of food on which animals do not naturally feed are not dissolved when introduced in these balls into the stomach; that if tubes or balls, for example, containing flesh, fish, grass, or herbs, be introduced into the stomach of a sheep, the latter are completely dissolved, while the former are not altered. The experiment was repeated on the ox with a similar result ; and hence it appears, that in those animals which usually feed on vegetables, animal food is not dissolved by the gastric fluid. Spallanzani, however, obtained a result somewhat different ; in animals which feed principally on grain, as ducks, hens, and turkeys, flesh introduced in tubes into the stomach being dissolved *, while in those which feed usually on flesh, as the crow, farinaceous grains, previously bruised and introduced in tubes, were likewise dissolved †. These animals, however, do not seem naturally much limited to one kind of food, but can subsist on very different substances. And

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* Dissertations, vol. i. p. 36.

† Ibid. p. 65.

it is admitted by Spallanzani, that some species, as birds of prey, are incapable of digesting vegetables *. It therefore rather appears, that the solvent power of the gastric fluid is in a great measure limited to the kind of food on which the animal naturally subsists, though the stomach is undoubtedly capable of in some measure adapting itself to the food received, so that the animal can at length be brought to be nourished by, and even to relish, substances the most opposite to those on which it naturally feeds. In those animals which feed both on vegetable and animal matter, as in man, both are dissolved by the gastric juice.

The solvent power of the gastric fluid is very well shown by its action on the stomach itself; it frequently happening, that an erosion, or even a solution of the depending part of the stomach, is discoverable after death, as Mr Hunter first pointed out †. And no fact better shows, how far the presence of vitality suspends or counteracts the usual chemical powers, since, during life, the stomach does not suffer from the action of this fluid. Stevens has however stated some facts to prove, that this is to be understood with some limitation, and that animals, even while alive, are in some cases subject to the process of digestion ‡.

These facts with regard to the solvent power of the gastric fluid are truly singular: they are such as could by no means be inferred from any quality that fluid is

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* Dissertations, vol. i. p. 217. 288.

† Philosophical Transactions, vol. lxii. p. 447.

‡ Dissertatio Inauguralis, p. 58.

known to possess, or from any other chemical agency it appears to be capable of exerting: they admit, therefore, of no explanation, and, in our present imperfect knowledge of its nature, must be received merely as ultimate facts.

SECT. VII.

OF BILE. BILIARY CALCULI.

Bile is a fluid secreted by the liver from the venous blood which has circulated through the abdominal viscera: it enters the intestines, and appears designed to serve some important purpose, from the large quantity of it secreted. It has generally been considered as an assisting agent in the process of digestion, or at least in the formation of chyle; and, in support of the latter conclusion, the fact has been generally stated, that no traces of the chyle are to be discovered previous to the intermixture of the bile with the digested food. It is no argument against this opinion, that the bile cannot be discovered by any of its properties in the chyle; for these may be changed by the combination, or some of its principles only may enter into the composition of that fluid, while others may be and undoubtedly are discharged as excrementitious. The singularity deserves to be remarked, that it is formed from venous blood, while the other secretions appear always to take their origin from arterial blood. This deviation, performed too by a particular apparatus, would lead to the conjecture, that a large proportion of carbon is necessary to its constitution; and it will accordingly appear from its analysis, that its principal solid ingredient is highly inflammable, and is very similar in its properties to the vegetable resins, in the composition of which we know carbon and hydrogen predominate. Fourcroy has even supposed, that that portion of it which is excrementitious is designed to convey an excess of hydrogen, and we may add, perhaps, of carbon, from the system; and under this point of view, which is not improbable, it may be regarded as subordinate to respiration, and as freeing the blood from principles which could not, without inconvenience, be fully abstracted by the action of the air.

The bile, when first secreted, is perfectly liquid, and, in this state, a portion of it constantly flows into the upper part of the intestinal canal. But in many animals, there is also a particular reservoir, the gall-bladder, into which a quantity is received, which from absorption becomes more thick, and which occasionally flows into the intestines. The qualities of the bile do not seem to be otherwise much altered in this organ, and its inferior importance is sufficiently demonstrated by the fact, that in many even of the more perfect animals it is altogether wanting. It is this cystic bile, however, as it is named, or bile collected in the gall-bladder, that has been generally examined, as it is that which is most easily procured.

It has always a certain degree of tenacity, more or less according to the time during which it has been retained in the gall-bladder, and, no doubt, also according to the energy of absorption. It feels unctuous, or rather soapy: its specific gravity is rather greater than that of water: its colour is green, with more or less of a yellow shade, and, in some animals, is nearly pure yellow: its odour is faint, and rather aromatic: its taste is extremely bitter, this bitterness being strong even in its most dilute state, and becoming intense when the bile, from stagnation, is thick and viscid.

Bile, from its obvious importance in the living system, has often been submitted to chemical examination, and a number of important facts with regard to it are now ascertained. For these we have been principally indebted to a series of experiments by Cadet* and by Ramsay †.

Bile left exposed to the atmosphere at a moderately warm temperature, soon suffers spontaneous decomposition; it emits a fœtid odour, and seems to pass into a state of putrefaction.

When exposed to a gentle heat, a large quantity of water, about 90 parts from 100, pass over; this water has the odour of the bile, but not its taste. The residual matter is thick and tenacious, of a dark brown colour, deliquescent and readily soluble in water; when kept for some time, it acquires a peculiar smell similar to that of ambergrise or musk: bile itself, too, acquires this smell on being kept, and communicates it to the water distilled from it. When the extract of bile, as the substance which is obtained by evaporation of the watery part is named, is exposed to a heat gradually raised, it is decomposed; a portion of water having a fœtid odour, and containing sulphuretted hydrogen, distils over; a liquid next passes, brown and very fœtid, and containing carbonate and acetate of ammonia; this is succeeded by an oil, at first thin and light, but which soon becomes thick, brown, and empyreumatic; more carbonate of ammonia sublimes, and there passes over a large quantity of elastic fluid, consisting of carbonic acid, carburetted and sulphuretted hydrogen gases. There remains a black spongy charcoal, which burns easily, and which, when left exposed to the air, affords an efflorescence of carbonate of soda. By incineration, there is obtained from it carbonate of soda, amounting to nearly half its weight, with a little muriate of soda, and some traces of iron *, and, according to Fourcroy, phosphate of soda and phosphate of lime. The dry matter obtained by the evaporation in this experiment takes fire if heated under free exposure to the air, and yields the same salts after the combustion, and, according to Thenard, a small portion of sulphate of soda.

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* Mémoires de l'Acad. des Sciences, 1767.

† Dissertatio Inauguralis, Edin. 1757.

Bile mixes readily with water in every proportion, and even in its inspissated state is readily dissolved by it. The solution changes the colour of violet, or mallow, to a green, indicating the presence of a free alkali.

The acids decompose bile. If a few drops of acid be added, little or no precipitation is occasioned, but a liquor of a reddish tint is obtained. If more acid, however, be added, a copious precipitate is formed of a greenish colour, especially when thrown down by muriatic acid; after some hours, as Cadet observed, much of this coagulum disappears, and there remains on the filtre a substance with a slight greenish tinge, and which, as is immediately to be observed, is very similar in its properties

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* Cadet, Mémoires de l'Acad. des Sciences, 1767, p. 351.

to albumen. The liquor obtained clear by filtration, has an extremely bitter taste; when evaporated, it deposites flakes, tenacious and inflammable, melting and burning when kindled, with much smoke like a resin, and soluble in alkohol. The liquor poured off from this precipitate contains soda, as it affords, by evaporation, the salt formed by the union of soda with the acid that has been employed in the experiment *.

These phenomena are best produced by the muriatic acid; the other acids produce effects in some measure peculiar. Concentrated sulphuric acid separates from it dense flocculi, and gives it a deep colour; diluted sulphuric acid renders it intensely green. Muriatic acid also precipitates it of a green colour, which from heat assumes a violet tinge. Nitric acid precipitates it green in the cold, but, when heated, assumes a red, and ultimately a grey colour; by evaporation it assumes a golden yellow colour, and the bile is converted partly into oxalic and prussic acids. Oxymuriatic acid whitens it and renders it turbid, by coagulating its albumen, and at the same time it converts its resin into a white fatty substance †.

The action of alkohol on bile affords results which point out still more clearly the nature of its immediate principles. When the alkohol is poured upon it, a coagulum is immediately formed, which floats in a liquid of a green colour. When this is separated by filtration, there remains on the filtre a white viscid substance, having scarcely any bitter taste and very putrescible, approaching therefore closely in its properties to albumen,

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* Cadet, Mémoires de l'Acad. des Sciences, 1767, p. 340.

† Fourcroy, ibid. 1789, p. 315.

and which has hence received the name of the Albumen of Bile. It can likewise be separated, though imperfectly, by heat, bile becoming thick when its temperature is raised to 170°, independent of any evaporation; and it is it, as has already been remarked, which forms the basis of the coagulum separated by the acids.

When the filtered liquor obtained in the coagulation of bile by alkohol is examined, it is found to retain the green colour and the very bitter taste of the bile itself. Being evaporated, it affords a concrete substance inflammable, fusible at 120°, soluble again in alkohol, and precipitated by the affusion of water [*]. From these properties, in which it approaches closely to the vegetable resins, it has been named the Resin of the Bile, and it appears to be the principle in which the odour, taste, and probably the most important properties of the bile reside. As it exists in the bile in combination with an alkali, some chemists have considered it as an oily principle, but resins are equally capable of combining with alkalis, and as this substance can be obtained solid without being unctuous, while it has also the pitchy tenacity and lustre, it approaches nearest in its characters to resin.

Besides these principles, Cadet observed, that there exists in the bile a kind of saccharine matter, which approached in its properties to the sugar of milk. He remarks, that Verheyen had alluded to the saccharine taste which is found in the bile when it has thickened by evaporation, and again dissolved in water; but the principle on which this depends, had not been discovered prior to his researches. He recognised it in different experiments. Thus, when bile was decomposed by muriatic acid, and the muriate of soda obtained by evaporation of the residual pure liquor, he found among the crystals of this salt, another matter in trapezoidal crystals, in which he observed the resemblance in taste to sugar of milk. And he also procured it by decomposing bile by nitric acid; it remains in the residual liquor when the coagulum has been separated, united with a portion of the oily or resinous matter; on saturating this liquor with an acid, this saccharine salt, as Cadet regards it, is precipitated, the alkali attracting the acid and the oily matter. It has been more lately investigated by Thenard *. On pouring into bile sub-acetate of lead, that is, acetate of lead boiled with about one-sixth of its weight of litharge, the whole of the albumen and oil (or resin) were precipitated; the liquor being filtered, the sub-acetate of lead was decomposed and separated from it by sulphuretted hydrogen; and by evaporation of the liquid after this operation, a substance was obtained, the flavour of which was at once saccharine and acrid. It being supposed to be still combined with saline matter from the bile, it was again precipitated by sub-acetate of lead; the precipitate, as it is expressed, was dissolved in vinegar to free it from the sulphuretted hydrogen, (implying probably, though this is not stated, that the combination of it with the salt of lead had been decomposed by this re-agent): it was then filtered and again evaporated. Thus obtained, as Thenard conceived, in a state of purity, he found

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[*] Saunders on the Liver, p. 110.

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* Nicholson's Journal, vol. xii. p. 270.

it to be soluble in water and in alkohol; not precipitated by common acetate of lead, but by the sub-acetate: it does not ferment with yeast, gives no ammonia by distillation, and is not affected by the infusion of galls.

Its most important property is that of dissolving the resinous, or, as Thenard calls it, the oily matter of the bile. This matter had always been supposed to be dissolved by the alkali which experiments proved the bile to contain, and from which the saponaceous quality of this fluid was supposed to be derived. But, according to Thenard, the quantity of alkali is not sufficient for this purpose; on the other hand, the saccharine matter alone would also be insufficient, as it only renders soluble about three-fourths of its weight of the resinous matter, while in the bile their weights are about equal; he supposes, therefore, that the resinous matter, saccharine substance, and soda, form a ternary soluble combination, which, with a little albumen and certain salts, constitute the bile.

The saline substances which the bile contains, are, besides the soda, the existence of which has been already stated, muriate, sulphate, and phosphate of soda, phosphate of lime, and oxide of iron; and he gives the following as the proportions of the immediate principles of this fluid.

Water,	700	parts.
Oily or resinous matter,	43	
Saccharine substance,	41	
Animal substance or albumen,	4	
	788	parts.

	788 parts.
Soda,	4
Muriate of soda,	3.2
Sulphate of soda,	0.8
Phosphate of soda,	2
———— lime,	1.2
Oxide of iron,	0.5
	799.7 parts.

Dr Saunders, however, it is to be remarked, could not detect muriate of soda in the bile by the test of nitrate of silver *.

Scarcely any thing is known with regard to the varieties of the bile in different animals: that of fishes is said to be less bitter than that of quadrupeds, and of a deep green colour. There is every reason to believe, that it is subject to considerable alteration from morbid secretion.

THERE are frequently formed in the gall bladder small concretions, derived, no doubt, from the changes the bile suffers while it remains in that organ. These have been named Biliary Calculi; and have been repeatedly subjects of chemical investigation. They are not altogether uniform in their appearance, but vary in their colour, texture, and hardness, and in their chemical characters.

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* Saunders on the Liver, p. 107.

The most common kind are of a lamellated structure, or composed of a substance having much resemblance to the animal fat named Spermaceti, disposed in crystalline laminæ. This peculiar matter appears first to have been taken notice of by Poulletier de la Salle. He found, that when these calculi were digested in alkohol, the liquid, on cooling, deposited brilliant crystalline flakes. Fourcroy, examining this matter[*], found, that it had a close resemblance in its properties to that species of animal fat which he has distinguished by the name of Adipocire, and of which spermaceti, as well as the fatty matter formed from animal substances under certain circumstances, are varieties. The characters of this substance are sufficiently precise. It melts, but requires a heat superior to that of boiling water: in fusion, it has a smell like wax, and on cooling, forms a substance which breaks into crystalline laminæ. It is not soluble in alkohol in the cold; but when the alkohol is boiled on it, it is dissolved in a proportion, according to Fourcroy, of one part in nineteen,—according to Dr Bostock, one in thirty[†]. The solution, when it cools, deposites light brilliant scales. It is also soluble in ether in the cold, and more abundantly if the ether be heated. Oil of turpentine dissolves in general biliary calculi; and according to Gren, it dissolves those which consist almost entirely of this peculiar matter; yet Dr Bostock has remarked, that oil of turpentine acts on it with difficulty, and, even when digested with it at a boiling heat, dissolves it in a small degree only. Pure soda and potassa dissolve it completely, and reduce it to a saponaceous state. Ammonia, as Dr Bostock has remarked, exerts little action on it, except when boiling. Nitric acid dissolves it, and, according to Fourcroy, converts it into a species of liquid similar to the oil of camphor. This, as Dr Bostock has remarked, becomes concrete, but without any crystalline structure, and is more soluble in ether and the alkalis than the original matter.

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[*] Mémoires de l'Acad. des Sciences, 1789, p. 323.

[†] Nicholson's Journal, 8vo, vol. iv. p. 137.

This substance, Fourcroy has observed, is contained in greater or less quantity in nearly all the human biliary calculi, more or less intermixed with other matter, but still so far predominant as to form their basis. Hence they partake of its properties; are fusible, inflammable, and more or less soluble in the re-agents which dissolve it. Their texture is laminated or radiated: some are found in which it is nearly pure, and which consist of layers, soft and brilliant; in others, it is intermixed with a yellowish or greenish matter, probably inspissated bile; and in some, this matter is in so large a proportion, that the adipocire is disguised, and is discovered only by its deposition, when the calculus has been dissolved by hot alkohol; and often the calculus consists of layers, which, from their colour, appear to consist of these principles in different proportions. It is not improbable, that this peculiar matter is formed by changes which take place in the oily or resinous principle of the bile.

Other calculi are sometimes found, particularly in the gall-bladder of quadrupeds, which have been supposed to consist chiefly of inspissated bile: they are granulated, irregular, and various in their consistence and form. It is to be remarked, however, that though this kind of matter, forming the basis of these, and more or less mixed with the adipocire in other biliary calculi, may be derived from inspissation of the bile, yet it must have undergone some farther change; for, as Dr Bostock has remarked, it is nearly insoluble both in boiling water and in alkohol.

To point out the distinctions among all these calculi from their mechanical structure, is foreign to their chemical history.

SECT. VIII.

URINE. UREE. URIC ACID. URINARY CALCULI.

THE fluid, secreted by the kidneys, is excrementitious, or is designed to convey from the body matter which, if retained, might prove injurious. It contains more saline substances than any other secretion, mixed, however, with other animal principles, which give it appropriate characters. Some of these are even peculiar to it; and hence its chemical history is of much importance, and has been the subject of many laborious investigations. To these we owe the discovery of phosphorus, which was first obtained from this fluid; and more lately, the discoveries of the principle named Urée, and of the Uric Acid. Margraaf began the scientific investigation of its composition. Some facts were discovered by Rouelle[*]. Scheele discovered the uric acid, and pointed out the existence of some other principles[†]. Cruickshank added a number of important facts on the modes of analysis, pointed out more clearly the principles existing in urine, both in a healthy and a morbid state, and distinguished the peculiar animal matter which it contains[‡]. The nature of this principle, and its peculiar characters, were more amply developed by Fourcroy and Vauquelin; and a very full view has been given of the chemical history of urine, in two memoirs by these chemists[||].

The colour of urine, when it is newly discharged, is a pale yellow: its odour is peculiar, but not strong nor fœtid, such as it becomes when it has stood for some time: its consistence and specific gravity are rather greater than those of water: it is perfectly transparent, but becomes more or less turbid as it cools. These qualities, however, are always liable to variation, according to the length of time it has remained in the bladder after having been secreted, and according to the diet, the quantity of drink, and other circumstances which influence the secretion.

Urine, examined when immediately discharged, is in general sensibly acid, and reddens the infusion of litmus. This acidity it owes to the presence of phosphoric acid, of benzoic acid, and of an acid peculiar to urine and urinary calculi, and hence named Lithic or Uric Acid. But in a very short time, from the spontaneous decomposition of a principle contained in it, that named Urée, a quantity of ammonia is evolved, which not only neutralizes these acids, but renders the urine alkaline. Previous to this, however, and as the urine cools, it deposites, unless it has been in a very dilute state, part of the uric acid which it contains, in minute crystals of a reddish colour, and in some states of the system this deposition is even abundant, forming principally what is named the Lateritious Sediment. The deposition of this, however, is soon interrupted, from the evolution of ammonia, which neutralizes it; urate of ammonia is deposited; the free phosphoric acid is likewise saturated; the proportion of phosphate of ammonia is thus increased, and the neutral phosphates of lime and of magnesia, which were retained in solution by the free acid, are deposited, the latter attracting a portion of ammonia, so as to form a triple phosphate of ammonia and magnesia. The benzoic acid passes to the state of benzoate of ammonia. As the decomposition proceeds, the ammoniacal odour becomes strong, and at length the urine is highly alkaline, from the presence of carbonate of ammonia, so as to change the vegetable colours to a green, and even to effervesce with acids. In ths state it likewise, according to Fourcroy and Vauquelin, contains, neutralized by ammonia, a portion of acetic acid, derived, as well as the ammonia and the carbonic acid, from the decomposition of the urée. If kept until the whole of this urée has been decomposed, there may be obtained from it, by evaporation, its remaining salts, which are principally phosphates and muriates, with bases of ammonia, soda, magnesia, and lime. During the progress of this spontaneous decomposition too, a mucous or albuminous animal matter is also deposited in flocculi, at first very light and of a pale colour, but becoming more dense and dark; and in some states of the urine, the proportion of this is even greater than of saline matter: Sometimes the ammoniacal pungency is much less strong, or is scarcely apparent, and a mouldiness or acescency rather marks the decomposition.

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[*] Journal de Médicine, 1773.

[†] Chemical Essays.

[‡] Rollo on Diabetes, 2d Edit.

[||] Mémoires de l'Instit. National. tom. ii. and iv.

The acid contained in recent urine in a free state, is principally the one denominated Lithic or Uric, and which though present in very variable quantities, is contained more or less in all urine. Even when it is not spontaneously deposited, it may be detected by its tests, particularly by the pink colour which it gives with nitric acid; it is often made to precipitate, by concentrating the urine by evaporation, or it may be thrown down by the addition of an acid. With uric acid, there is almost always present a portion of free phosphoric acid, which is, however, soon saturated by the evolution of ammonia. A small portion of benzoic acid is also usually present, as Scheele discovered; and in the urine of children, as well as that of horses and cows, it is often contained in considerable quantity; in which case the other acids exist in smaller proportion, and the urée appears also to be defi~~cient.~~ Hence, by mere evaporation of the urine, and the application of a sufficient heat to the residual matter, the benzoic acid is sublimed. It is also precipitated when Muriatic acid is drop into the urine, evaporated to the consistence of syrup.

When urine is exposed to a gentle heat, water, holding carbonate of ammonia in solution, is evaporated; the proportion of which increases, as the evaporation proceeds. The liquid becomes turbid, darker in its colour, and stronger in its odour; and a flocculent matter, with a whitish powder, are precipitated: the former being supposed, by Fourcroy and Vauquelin, to be albumen, the latter being phosphate of lime and uric acid. When reduced to the consistence of thin syrup, if put aside, it passes to the state of a confusedly crystallized mass. If the liquor poured from this be again evaporated, this is repeated; and in this way several successive formations of crystals, irregular, and of a brownish colour, take place, leaving at length a liquor, deep coloured and of a thick consistence, in which the urée exists in a state of solution.

The saline matter obtained from urine by evaporation, has long been a subject of chemical investigation: it was known to the alchemists, and it engaged the attention successively of Margraaf, Pot, Rouelle, and Scheele. It had received the absurd name of Microcosmic Salt, and, from its fusibility, had also been named Fusible Salt of Urine. It was known to afford phosphorus by distillation. Margraaf recognised in it the presence of muriate of soda and phosphate of ammonia, and likewise the phosphate of soda; without, however, being fully acquainted with the nature of this last salt; he observed too, that it is the phosphate of ammonia alone which affords phosphorus, in the usual process of obtaining it from urine. Rouelle distinguished more clearly the phosphates of ammonia and soda, and described the methods of separating and purifying them. He announced also the presence of muriate of potassa, which had been before confounded with the muriate of soda, and which, it now appears, is present even in larger quantity than that salt. He supposed, that he had likewise extracted sulphate of soda; but as this has not been found by other chemists, there is reason to believe that he had been deceived, and had mistaken for it the phosphate of soda, or, as Fourcroy has observed, the triple phosphate of ammonia and magnesia. The sulphate of lime, which he also supposed he had discovered in this saline mass, it appears from the subsequent discovery of Scheele, is phosphate of lime. Fourcroy and Vauquelin have since discovered the phosphate of magnesia. These salts then,—the phosphate of soda, the phosphate of ammonia, phosphate of magnesia, phosphate of lime, muriate of soda, muriate of potassa, muriate of ammonia, and the triple compounds of phosphate of soda and ammonia, and phosphate of magnesia and ammonia, with a portion of uric acid, more or less saturated with ammonia, and urée, compose the crystallized mass obtained by the evaporation of urine. They exert, it is to be remarked, mutual affinities, in consequence of which their perfect separation is difficult, and they even modify their respective properties: the muriate of soda, for example, in crystallizing, takes the form of an octaedron, and not, as when pure, that of a cube; and the muriate of ammonia, instead of appearing under its usual form of a prism, crystallizes in cubes. These modifications, according to Fourcroy and Vauquelin, are owing principally to the action of the urée on the saline matter. It is also to be observed, that all these salts do not pre-exist in the urine; those containing ammonia derive this alkali principally from its formation during the evaporation.

It is difficult to determine the proportions of these to each other, as they are liable to considerable variation from the circumstances influencing the secretion. Mr Cruickshank, in his analysis of urine, undertaken in the course of Dr Rollo's investigation of the nature of diabetes, has given the most precise information on this point, and indeed the most valuable information we have with regard to the analysis of urine *. "By evaporation, 36 oz. yield a residuum, varying from one ounce to one and a half; this consists of the muriates of potash and soda, the phosphates of soda, lime, and ammonia, the phosphoric and lithic acids, with animal extractive matter. Their relative proportions in a healthy state may be nearly as follows:

	oz.	dr.	gr.
Muriatic salts,	0	1	0
Phosphoric salts,	0	3	50
Lithic acid and phosphate of lime, with excess of acid,	0	0	25
Animal extractive matter, (urée),	0	3	40

"The neutral salts, when purified by crystallization, are generally very fusible; but this circumstance varies much, according to the greater or less proportion of phosphoric salts, more particularly the phosphate of ammonia, on which their fusibility in a great measure depends: instead of melting, this saline matter sometimes decrepitates

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* Rollo on Diabetes, 2d Edit.

when suddenly heated, owing to an excess of the muriatic salts: of these last it may be observed, that the muriate of potash is in general the most prevalent, and is easily distinguished from the muriate of soda, by its crystallizing in some degree by cooling, and by its affording cream of tartar on the addition of acid of tartar.

" In recent urine, the ammoniacal salts bear a very small proportion; but when it has become stale or putrid, they are much more abundant. The phosphate of ammonia is the principal, although we have likewise met with the muriate of ammonia.

" The lithic acid and phosphate of lime are generally deposited, at least in a great measure, after the urine has become cold, and stood for some time: the quantity of the first varies exceedingly, but that of the last we have found, for the most part, nearly the same, the proportion being about one grain to two ounces.

" These substances may be easily distinguished, by dissolving them in twice their weight of nitrous acid, diluted with a little water, and evaporating to dryness: the dry mass, when hot, will assume a beautiful deep rose or crimson colour, when the lithic acid is present, but will continue white if heated even to redness, or have only a slightly greenish tinge when there is nothing but phosphate of lime. Their relative proportions may be ascer~~tained by~~ exposing the mixed mass for some time to a red heat in a crucible; in which case, the lithic acid will either burn out or evaporate, leaving the phosphate in a pure state.

" The quantity of extractive matter is more variable than that of any other substance; hysterical, or crude urine (as it has been called), containing hardly any, while that of concoction abounds with it."

If the entire mass of urine be at once evaporated, and the solid matter be urged by a strong heat, it affords very fœtid carbonate of ammonia in large quantity, with a little prussiate of ammonia, an empyreumatic oil, gases composed principally of carbon and hydrogen : muriate of ammonia is also sublimed ; and towards the end of the process, if the heat be raised high, a small quantity of phosphorus distils over, produced by the decomposition of the phosphoric acid in the phosphate of ammonia. It was by this method that phosphorus was procured by Kunckel and Boyle. The coal which remains at the end of the process contains the salts which have not been decomposed,—muriate of soda, and phosphates of soda and lime.

The action of different re-agents on urine is instructive, as leading at once to a knowledge of a number of the principles which exist in it, some of which could not otherwise be easily recognised. The principal accurate observations on the effects of these are those of Scheele, Cruickshank, Fourcroy, and Vauquelin.

The greater number of the acids in general produce little sensible effect upon it in the healthy state. The oxalic acid only gives a precipitate, by combining with the lime of the super-phosphate of lime which recent urine contains. If it contain benzoic acid, the muriatic acid is said to precipitate it. If it be much loaded with urée, nitric acid throws down a scaly precipitate of a pearly lustre. And, in certain morbid states, as in dropsy, the a-acids sometimes occasion a milkiness, or even a coagulation of the urine, from albumen being contained in it.

The fixed alkalis, added to urine, throw down a slight precipitate, which is phosphate of lime, the alkali saturating the excess of phosphoric acid by which this was kept dissolved. About 2 grains, according to Cruickshank, are obtained from 4 ounces of urine. The watery solutions of lime, barytes, and strontites, produce still more copious precipitates, as the salts they form with the phosphoric acid, with which they unite, are insoluble. The fixed alkalis and lime disengage at the same time an ammoniacal odour, by decomposing the phosphate of ammonia, and partly, perhaps, by causing a formation of ammonia from the elements of the urée.

The nitrates and muriates of barytes, strontites, and lime, form precipitates, by decomposing the phosphates contained in urine; and they may conveniently be employed to discover the absolute quantity of this acid, the precipitate being collected, weighed, and dried. Four ounces of healthy urine, according to Cruickshank, yield with muriate of barytes a precipitate of 13 grains, consisting of phosphate of barytes, produced by the decomposition of the phosphates of soda and ammonia; a precipitate of 13 grains indicates a quantity of these, or of what has been more peculiarly named Microcosmic ~~Salt, equivale~~nt to 25 grains; and, of course, this test may shew the proportion of these salts in the urine. The nitrates of silver, quicksilver, and lead, occasion a copious precipitation, the precipitate consisting principally of phosphoric acid, but partly also of muriatic acid, with the metallic oxide. If nitrate or acetate of lead be employed, the muriate of lead, it was remarked by Cruickshank, may be dissolved, by boiling in 18 or 20 times its weight of water, the phosphate of lead remaining undissolved, and thus, by weighing the original precipitate, and the loss it sustains in this operation, the quantities of phosphoric and of muriatic acids in the urine may be determined. "Four ounces of healthy urine, treated in this way, yield a precipitate of 31 grains; this being digested in distilled water, 7 grains were taken up; the remaining 24 were found to be phosphate of lead, equivalent to 23 or 24 grains of microcosmic salt *.

Infusion of tannin almost always detects in urine a little gelatin, by the cloudiness it occasions or the precipitate it throws down; about 4 grains are usually obtained from 4 ounces of healthy urine, and, in certain morbid affections, especially where the digestive organs are impaired in their power, the quantity of gelatin discovered by this test is considerable. Some chemists have supposed, that the precipitate tannin occasions may be owing to the presence of albumen; and Fourcroy and Vauquelin have observed, in proof of this, and of the presence of this principle, that flakes are formed in urine merely by heating it; but, with regard to this, there is still some obscurity, for no coagulation is produced in it either by acids or by alkohol, which there ought to be, did it contain albumen.

It has been stated, in the preceding account of the analysis of urine, that when it is evaporated, so as to obtain the greater part of its saline ingredients by precipitation,

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* Cruickshank, Rollo on Diabetes.

or crystallization, there remains, at length, a liquid of a dark colour, of a thick consistence, and uncrystallizable, having the more evident urinous properties. This liquor is principally a solution of the peculiar animal principle contained in urine. Obtained by evaporation, in a state of more or less intermixture with the saline ingredients, it was named, by the older chemists, the Extract of Urine. It had been distinguished more particularly by Rouelle, and considered by him even as a distinct substance*. There may be obtained from the urine, he observes, besides the saline matter, two substances, one soapy, the other extractive; the first is very soluble in alkohol, the second is insoluble. The soapy substance, (which is evidently the urée), he describes as of a brown colour, a fœtid odour, an unctuous consistence, crystallizable like a saline body, not easily susceptible of exsiccation, attracting humidity from the air, and giving by analysis more than half its weight of volatile alkali, a little oil, and muriate of ammonia. It is evident, observes Vauquelin, that Rouelle, by these characters, had very well distinguished a peculiar principle existing in urine.

His observations, however, were neglected by succeeding chemists; and the existence of this principle may be said to have been re-discovered by Mr Cruickshank, who obtained it by a peculiar method, and considered it under a ~~point of view altogether~~ different from that exhibited by Rouelle†. "If to an ounce," says he, "of the extractive matter of urine, there be added an ounce of the concentrated nitrous acid, diluted with an equal quantity of water, a violent effervescence, accompanied with heat, and the disengagement of nitrous gas, will take place; when the action has ceased, and the liquor become cold, a number of shining scales, or crystals, resembling the acid of borax, will be deposited, which, when well dried on blotting paper, will be found to weigh from 5 to 7 drachms, or sometimes more, the proportion varying according to the quality of the extract, and the method of conducting the process.

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* Journal de Medicine, 1773.

† Rollo on Diabetes, 2d edit.

" The figure of these scales appears to be that of flat rhomboids; they have a smooth greasy feel when pressed between the fingers; are soluble in much greater quantity in hot, than cold water, and also in some degree in alkohol; although repeatedly washed with this fluid, and dried on blotting paper, they still retain acid properties, and strongly redden the syrup of violets; they are readily taken up by the sulphuric and muriatic acids without commotion; but, with the nitrous acid, they produce a kind of effervescence, and appear to be in some measure decomposed; they combine with the mild alkalis with effervescence, and form very soluble neutral salts, whose properties have not been sufficiently examined. Their solution in water does not precipitate lime-water, nor the muriates of lime or barytes, nor the nitrates of silver or mercury, in any sensible degree, nor has it any effect upon the sulphate of iron or acetate of lead; they do not, therefore, contain phosphoric or oxalic acid; when thrown upon a red hot iron, they melt and evaporate in white smoke, leaving a very small quantity of a charry residuum, by no means difficult to incinerate; but when exposed to an intense heat, they burn with a reddish flame, and a kind of detonation somewhat similar to the nitrate of ammonia.

"From these experiments, it would appear, that this substance is an animal acid hitherto unknown, and whose basis exists in this extractive matter."

Fourcroy and Vauquelin, in a dissertation on the urine of the horse *, prior to the publication of Cruickshank's experiments, had observed, that if to the liquor remaining after the separation, by evaporation, of the saline substances, and of the benzoic acid by muriatic acid, there be added nitric acid, a precipitation immediately ensues of slender brilliant crystals, so as to form, in a short time, a concrete white mass, which at length became of a brown colour. This, after a slight examination of its properties, they considered as a new principle, before unknown to chemists: it continued to engage their attention; and, in a subsequent memoir †, they gave a very ample detail of the facts they had discovered with regard to it. They gave to it, from the secretion in which it is principally found, the name of URÉE.

The following is the method by which these chemists obtained this substance in an insulated state.

Urine is evaporated, by a very gentle heat, to the consistence of thick syrup. It thus acquires a dark brown colour, and a foetid ammoniacal smell. On cooling, it concretes into a confusedly crystallized mass, consisting of a mixture of its salts with the urinary matter. To ob-

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* Mémoires de l'Institut. National, tom. ii. p. 443.

† Ibid. tom. iv. p. 402.

tain this, there was poured on this mass four times its weight of alkohol, in successive portions, heating them gently; the greater part is dissolved, and gives a dark brown colour to the fluid; there remains undissolved a saline matter nearly white. The solution contains the urée: it is distilled in a retort placed in a sand bath; the alkohol passes over fœtid and impregnated with carbonate of ammonia, and a portion of animal matter. The distillation is continued until the liquor is of the consistence of syrup; the alkohol is thus dissipated, and the matter, in cooling, crystallizes under the form of quadrangular plates, crossing each other, of a brilliant yellowish white colour. This is the Urée. It exhales a strong urinous odour: it has a degree of tenacity which renders it difficult to be cut or detached from the vessel in which it has been evaporated: it attracts humidity, however, from the air, and forms a thick brown coloured liquid; and it dissolves rapidly in a very small quantity of water, producing, during its solution, a very sensible degree of cold: it is less soluble in alkohol, but its solution in this fluid, saturated by being made with the assistance of heat, gives, on cooling, crystals more readily than the watery solution. Its solution in water, when concentrated, is of a brown colour; which, by dilution, passes through the different shades of orange, yellow, and lemon colour, so as to resemble urine in the various states in which it occurs. And they regard it, with justice, as the principle in which the most characteristic properties of this animal fluid reside.

Fourcroy and Vauquelin have given, in their memoir, a very detailed account of the chemical properties and relations of urée, from which I give an abridged statement of the principal facts.

Exposed to heat in a retort connected with an apparatus adapted to collect the products, it melts quickly, and a vapour is disengaged, which condenses in the neck of the retort into a crystalline deposite, having all the appearances of benzoic acid, which has probably been contained in the urée, and derived from the urine. When this has ceased, carbonate of ammonia sublimes; and the sublimation of it continues, without interruption, to the end of the experiment; no oil is condensed, nor even any watery liquor, but merely the salt tinged brown, and of a very fœtid odour. As the heat is raised, this odour becomes more insupportable. The matter appears, at length, at the bottom of the retort in a dry state, black, and covered with a white crust; this sublimes, and is found to be muriate of ammonia. After exposure for two hours longer to the fire, the carbonaceous residuum gives, by lixiviation, a liquor smelling of prussic acid, and which precipitates, with the aid of an alkali, the solutions of iron, blue: it contains, too, muriate of soda, and a little muriate of ammonia. In burning it in an open fire, it disengages an ammoniacal odour, mixed with that of prussic acid. There remains, at length, a matter, amounting to about an hundredth part of the urée, white, acrid, soluble, which changes the vegetable colours to a green, and effervesces with acids, being, apparently, carbonate of soda.

In the progress of this decomposition, carburetted hydrogen gas, with perhaps a little carbonic acid and nitrogen gases, were likewise disengaged. In repeating the experiment, it was found, that 288 parts of urée gave 200 parts of carbonate of ammonia, 10 parts of carburetted hydrogen gas, 7 parts of residual charcoal, 68 parts of muriate of ammonia, acid of benzoin, and muriate of soda, with quantities too minute to be estimated of oil and prussic acid. The benzoic acid, muriate of ammonia, and muriate of soda, these chemists considered as contained in the urée, but probably foreign to its composition; hence, from the other products, it follows, that this substance is a compound of nitrogen, hydrogen, carbon, and oxygen; and the large quantity of ammonia which the analysis affords, proves, that, among these elements, the nitrogen is present in largest proportion. The proportions could not, from this experiment, be fixed, perhaps, with perfect accuracy; but, from the quantities of ammonia, carbonic acid, carburetted hydrogen, water, and charcoal produced, compared with the quantity of urée decomposed, they are stated by Fourcroy and Vauquelin at 39.5 oxygen, 32.5 nitrogen, 14.7 carbon, and 13.3 hydrogen; and admitting a correction of these, on account of the portion of water which might be supposed to have pre-existed in the matter, there is a reduction in the proportions of oxygen and hydrogen, and the nitrogen becomes, not only with regard to the characters it communicates, but in quantity also, the predominating ingredient.

So susceptible is this principle of decomposition, and so liable are its principles to pass into those combinations which form ammonia and carbonic acid, that, by merely distilling it with water, it is almost entirely converted into carbonate of ammonia. In subjecting to distillation a solution of two parts of urée in nine parts of water, the water passed over, charged with carbonate of ammonia, transparent and pure; the residual quantity became concrete on cooling, and with a browner colour, and less crystallized. On adding to this the same quantity of water as before, and repeating the distillation, another solution of carbonate of ammonia, tinged brown, was obtained. A third distillation gave a similar product, but of a deeper colour, as if it were oily, and from which a little charcoal was deposited. After these three successive operations, the urée had afforded more than half its weight of carbonate of ammonia, and yet its power of yielding this product was not exhausted; for although, when diluted with a fresh quantity of water, it gave indications of the predominance of acetic acid, yet it lost this acidity in four or five days exposure to a temperature of 77°, and again gave an ammoniacal water by evaporation, deposited some crystals of muriate of soda, and afforded a precipitate of urée with nitric acid. Thus, this principle is more susceptible of decomposition than almost any animal product.

When abandoned to itself in solution in water at a natural temperature, other affinities are exerted among its elements, and it passes into the acetous fermentation. The liquor, exposed in a vessel imperfectly closed, soon became turbid, a scum collected on its surface, bubbles of air continued to be disengaged, and a lighted candle let down into the upper part of the vessel was extinguished. It acquired a sharp acidulous but fœtid odour: at the end of three months, this fermentation had ceased: it was then subjected to distillation, twice the weight of the original matter, of sulphuric acid being added. A product, was obtained, containing acetic and also benzoic acid : the residuum contained sulphate of ammonia, and gave a precipitate of charcoal. Here, therefore, the elements of the urée had combined so as to form more acetic acid and less carbonic acid and ammonia than when heat was applied. When a little albumen had been added to the solution of urée, the phenomena of fermentation were still more strikingly exhibited ; and although acetic acid was formed, the product of ammonia was greater, so that the liquor was sensibly alkaline.

Urée, subjected to the action of acids, presents results altogether different from those exhibited by any other animal principle, and which throw light on its peculiar composition.

Its solution in water, mixed with a fourth of its weight of sulphuric acid diluted, gave no effervescence. The mixture, heated until it boiled gently, became covered with a layer of oily matter, black, and which became concrete on cooling. The liquid which had evaporated and been condensed during this action was of a yellow colour; particles of charcoal were diffused through it : its odour was similar to that of empyreumatic acetic acid, its taste hot and acrid. It reddened litmus, without precipitating the barytic salts, and therefore, though acid, contained no sulphuric acid. Saturated with lime, ~~it afforded~~ acetate and benzoate of lime ; the benzoic acid, according to the supposition of Fourcroy and Vauquelin, having been derived from the urine. The residual liquor contained much sulphate of ammonia. Hence, in the decomposition of the urée by the sulphuric acid, its elements had been combined so as to form principally an oil, acetic acid, and ammonia, a little charcoal being precipitated.

The manner in which nitric acid acts on urée is peculiar and singular, and altogether different from what would be expected from the known agency of this acid. Urée is extremely susceptible of decomposition; and nitric acid is, of any agent, that which acts with most energy in decomposing vegetable or animal substances; yet the urée is not decomposed by it, but rather enters into combination with it. The observation by Cruickshank, that a precipitate of shining scales or crystals is produced when nitric acid is added to urine concentrated by evaporation, has been already stated; and Fourcroy and Vauquelin have found, that the same appearance is produced still more distinctly with pure urée. When the nitric acid is added to a strong solution of it in water, there is an instant deposition of crystalline plates, white, brilliant, and pearly, which augments so rapidly, that the whole mixture nearly appears to be converted into this matter. These chemists sought to determine its nature. When heated gently, it softens and melts like oil, a brisk effervescence takes place, and it is in part converted into nitrate of ammonia. Hence they regarded it as a compound of the urée and nitric acid.

When the nitric acid is concentrated, and particularly when it is surcharged with nitric oxide, and when the urée is in a concrete state, the mutual action is attended with a brisk effervescence, and an evolution of heat; nitric oxide, nitrogen, and carbonic acid gases are disengaged, and there remains a white or yellowish concrete matter, with a few drops of a red liquid: if this residuum is heated, it detonates and inflames in the same manner as nitrate of ammonia. In this rapid action, then, the urée is decomposed. If the acid be diluted, and heat applied, it likewise suffers decomposition, but more slowly, so that the progress of the operation, and the products arising from it, can be more accurately observed. Fourcroy and Vauquelin found, that nitrogen and carbonic acid gases were first disengaged in large quantity, then nitric oxide, mixed with carbonic acid: an elastic fluid, similar to atmospheric air, having a sharp odour of prussic acid, likewise appeared, when the disengagement of nitrogen had ceased, and that of nitric oxide commenced: at the end of the second day, a gentle heat having been always applied, the matter having become thick, and furnishing scarcely any considerable vapour, took fire, with a violent explosion: there remained in the bottom of the vessel an oily carbonaceous matter, which gave to water with which it was lixiviated an odour of prussic acid and ammonia, as well as the property of precipitating the solutions of iron blue. A quantity of charcoal remained after the lixiviation; and there was condensed in the receiver a yellow liquor, very acid, on which floated a few oily particles having a penetrating odour. A considerable loss attended the operation; and hence the proportions of the products could not be determined so as to give any certain results; but, as Fourcroy and Vauquelin have observed, there is in this decomposition scarcely any sensible production of that fat matter, of the yellow bitter principle, or of the oxalic or saccho-lactic acid, which are so generally the products of the action of nitric acid on animal matter: the whole consists in the disengagement of nitrogen, and the formation of carbonic acid, prussic acid, and ammonia,—a result which shows clearly the predominance of nitrogen in the composition of urée; that, next to it, carbon is contained in largest quantity, and that the proportion of hydrogen is comparatively small.

Muriatic acid produces on this principle scarcely any effect, precipitating it only from its solution in alkohol in brown flocculi. Oxymuriatic acid, however, produces in it a decomposition somewhat peculiar. When the oxymuriatic acid gas is transmitted through its solution, it is absorbed in large quantity, the liquor becomes brown, flocculi of the same colour appear, which soon become yellow, and adhere to the sides of the vessel like a concrete oil. These become paler in their colour, small bubbles of air continued to be disengaged from them, even long after the transmission of the oxymuriatic acid gas had ceased: this air consisted of about one-third of it carbonic acid, and two-thirds nitrogen. The liquor, at the end of the experiment, contains a large quantity of muriatic acid, with a portion of undecomposed urée. It appears, therefore, as Fourcroy and Vauquelin have given the rationale of this operation, that the oxymuriatic acid had first decomposed part of the urée, by yielding to it oxygen; that it had likewise continued to re-act on the flocculi produced from this decomposition, and to disengage from them nitrogen, its oxygen at the same time combining with carbon; while the muriatic acid into which the oxymuriatic acid had passed fixed and retained in the liquor the greater part of the urée, protecting it from decomposition.

Urée is perfectly soluble in alkaline solutions, and, at the same time, is partially decomposed. When triturated with a solution of potassa, a strong ammoniacal odour is immediately exhaled; and as the same effect is produced by carbonate of soda or of potassa, by lime, barytes, and even by magnesia, it probably arises from the decomposition of muriate of ammonia, mixed with the urée. But besides this, when this principle, in its solid state, is triturated with potassa, dry and in powder, an energetic action is manifested; the temperature rises considerably; there is disengaged so large a quantity of ammonia, that it must be considered as formed by the combination of its elements: the colour, at the same time, deepens, and an oily-like matter appears on the surface. When heat is applied, even though the mixture has been previously diluted with 4 or 6 parts of water, the decomposition is rapid, and proceeds to a greater extent; pure ammonia, with a portion of carbonate of ammonia, are disengaged and absorbed by the water in the receiver: the residual matter, diluted with water, gave a violent effervescence on the addition of weak sulphuric acid; indicating, that part of the potassa was in the state of carbonate. A voluminous flocculent precipitate was at the same time deposited, having the properties of a concrete oil: and, in the last place, the liquor being submitted to distillation, afforded acetic and benzoic acids. The potassa, therefore, assisted by the heat, had decomposed the urée in a manner analogous to the sulphuric acid, or to that which this principle suffers spontaneously at a high temperature, the products being nearly the same,—ammonia, carbonic and acetic acids; and different from those which this alkali usually produces when it causes the decomposition of animal matter, particularly in the small proportion of oily matter that had been formed; a difference no doubt owing to the large proportion of nitrogen, and smaller quantity of hydrogen, in the composition of urée.

Urée has a singular effect on some of the neutral salts,—that of changing the form of their crystals. It had been long known, that if urine were saturated with muriate of soda, this salt was again obtained from it by spontaneous evaporation, not crystallized in its usual form of cubes, but in octaedrons: and Fourcroy and Vauquelin found, that by the same method muriate of ammonia crystallized, not in prisms, but in cubes. They further found, that this singular effect depends on the action of the urée; since it equally happens when the salts are dissolved with pure crystallized urée in water, and their solutions crystallized by spontaneous evaporation. The crystals always retain too, a brown colour, and when freed from the urée which thus appears to be combined in them, by sufficient exposure to a red heat, they again crystallize from a solution in water, in their usual form.

The solution of urée in water, decomposes some of the metallic salts. Those of the nitrates of silver and quicksilver, it precipitates white: that of nitrate of lead, it throws down of a yellowish brown, which may be redissolved, after some time, in a large quantity of water, and then appears, on evaporation, in brilliant silvery crystals.

Tannin changes a little the colour of a solution of urée, but does not precipitate it; a character by which this principle is well distinguished from the albuminous or gelatinous matter so frequently secreted with it.

This principle being so uniformly secreted in considerable quantity, and altogether discharged from the system, must necessarily be subservient to some important purpose in the animal economy. Fourcroy and Vauquelin, in conducting their investigation of it, advanced the theory, that it is designed to convey the redundant nitrogen from the system, as the secretion of the bile discharges the superfluous hydrogen, and the changes in the lungs, by respiration, perform the same office with regard to carbon. There is a degree of obscurity attending this theory, since the difficulty hitherto has been rather to account for the origen of the nitrogen in the system of animals, than to provide for its discharge. Yet it is no doubt true, that this element being contained in so large a proportion in urée, is proved to be uniformly discharged in considerable quantity; and this perhaps adds some force to the hypothesis, that nitrogen, by the series of chemical actions connected with animalization, is actually formed or evolved, and that in a system therefore liable to variations in its functions, we may look for a function by which its accumulation will be prevented. Under this point of view, the above theory might be regarded as probably just.

The tendency of this principle to pass to the state of ammonia, is probably frequently the cause of morbid changes to which the urine is liable; it may even be the cause, sometimes, of the formation of urinary concretions, for if the excess of acid in the urine be saturated by the production of this alkali, the albuminous or gelatinous matter which the acid held in solution will be separated; and if a partial deposition of phosphate of lime or mag nesia, or of uric acid, take place at the same time, as may happen from the same cause, the nucleus of a calculus may be formed. The cementing ingredient in many of these calculi, in the greater number indeed, appears to be this albuminous matter, which is separated from urine whenever its acidity is neutralized; and it cannot but be considered as probable, but that the formation of such calculi may depend on some operation of this kind.

The predominance of nitrogen in the composition of urée, it is remarked by Fourcroy and Vauquelin, explains very well the great advantage derived from the intermixture of urine in the materials of nitre beds, in the production of nitre; the presence of the vegetable matter so far altering the affinities, as to prevent or diminish the formation of ammonia, and cause part at least of its nitrogen to enter into combination with oxygen. And the large product of ammonia, from the distillation of urine, a process carried on, even in the large way, in the manufacture of muriate of ammonia, depends more, as they have remarked, on the decomposition of the urée, than on that of the ammoniacal salts which that fluid contains.

There still remains to be given, the chemical history of another substance always contained in urine, and nearly peculiar to it, the Uric Acid.

The discovery of this acid we owe to Scheele. In analyzing urinary calculi, he found, that all those which he had submitted to experiment, consisted principally of a substance sparingly soluble in water, but which, by boiling a large quantity of water upon it, might be dissolved, and afforded a solution which reddened the more delicate vegetable colours, and from which, on cooling, the greater part again separated in minute crystals. This he regarded as a peculiar acid: and he added the observation, that it is contained in all urine, and frequently in considerable quantity, so as to be deposited as the urine cools *. Bergman had likewise, in analysing urinary calculi about the same time with Scheele, observed this acid. It was made the subject of experiment by Dr Pearson †: several of its properties were pointed out by Fourcroy and Vauquelin: and Dr Henry has added much to our knowledge of these, and of its various combinations, and in a dissertation has given an excellent view of its chemical history ‡, from which I take principally the following facts.

From being considered as the basis of urinary calculus or stone of the bladder, it received the name of Lithic Acid; a name certainly improper, not only from the solecism which, as Dr Pearson observed, it involves, but as this substance is not confined to these concretions, but is also contained in urine, while there are urinary concretions, in which no sensible quantity of it can be detected. Hence the appellation Uric, which he suggested, is preferable.

There is a difficulty in procuring this acid pure: for as deposited from the urine, or as contained in urinary concretions, it is always in a state, either of combination or mixture; and it is generally in these states that it has been hitherto examined. The process given by Dr Hen-

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* Chemical Essays, p. 199.

† Philosophical Transactions, 1798, p. 37.

‡ Dissertatio Inauguralis, Edin. 1807.

s, to dissolve a calculus, of that kind which consists y of this acid, in a solution of pure potassa. Muriate or acetic acid is added to this solution of it, while any precipitate of a white colour is thrown down; this precipitate is to be washed repeatedly with tepid distilled water, and in order more completely to remove any foreign acid, a few drops of water of ammonia are added to the water with which it is first washed; and if any minute portion of albuminous matter has been precipitated with it, which sometimes happens, it is separated by pouring off the water in which the flocculi of this are suspended, while the heavier uric acid is allowed to subside *.

Uric acid obtained by this process, is in the form of a white powder, rough to the touch, but which yields easily to the pressure of the finger. It is altogether free of taste. It dissolves in 1150 times its weight of water at 21°, or in 1720 times at 60° †; a degree of solubility much less than what Scheele had stated, owing to his experiment having been made on it merely as forming part of a calculus; in which state, as Dr Pearson has remarked, it is much more soluble, no doubt from its impurity. The solution in hot water on cooling, deposites pellucid crystals, so small, that the form cannot be described. The infusion of litmus is reddened by this solution. Soap is decomposed by it, not indeed by adding a solution of the acid to a solution of soap in water, for from this addition no turbid appearance is produced; but by digesting the acid, in powder, with soap, and as much water as is

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* Henry, Dissertatio Inauguralis, p. 12.

† Ibid. p. 14.

required to dissolve it, the oil is separated, and a milky like liquor is produced *. It decomposes the alkaline sulphurets, precipitating the sulphur: and it combines directly with the alkalis, earths, and metallic oxides, the alkaline properties being neutralized in the combination. These properties, as Dr Henry has justly remarked, are sufficient to class it among the acids. Dr Pearson inferred from his experiments, that it did not redden the vegetable colours, nor decompose soap; and observing farther, that it is tasteless, scarcely soluble in cold water, not capable of uniting with the alkali of carbonate of soda, potassa, or ammonia, nor with the lime of lime water, nor with oxide of mercury; and that its combination with caustic soda, resembles soap more than any compound salt known to consist of an acid and alkali, inferred, that it cannot be regarded as an acid, but is to be considered as an animal oxide †. Some of these properties, however, are not strictly characteristic of acidity, and with regard to others, as that of not reddening the vegetable colours or decomposing soap, the observation appears to have been inaccurate. The acid powers, however, of this substance, are undoubtedly weak. It has been long known, that it is incapable of disengaging the carbonic acid from the alkaline carbonates, nor is it dissolved by them: it acts with no energy on the metals, nor does it precipitate any of the earthy or metallic salts.

The combinations of uric acid with the alkalis and alkaline earths are easily effected, by digesting in hot wa-

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* Henry, Dissertatio Inauguralis, p. 16.

† Philosophical Transactions, 1798, p. 27.

[illegible] the base with a quantity of the acid, more than sufficient for its saturation, straining the solution, and evaporating it as far as may be necessary with a gentle heat. Dr Henry has examined the general properties of these urates, as thus obtained, in a state of purity, and gives the following enumeration of them. They are tasteless, and, in external appearance, can scarcely be distinguished from the acid itself. Exposed to the air, they undergo no change, neither losing nor attracting water. They are very sparingly soluble in water. Urate of ammonia, contrary to what has been affirmed, is the most soluble, and, of it, an ounce of distilled water at 60 dissolves only 2 or 3 grains. The others, with regard to solubility, stand in the following order: urate of potassa, of soda, of lime, of strontites, of magnesia, of argil, and of barytes. If to the solution of any urate, any acid, the carbonic and prussic excepted, be added, the uric acid is precipitated in the state of a white powder. The alkaline urates are also precipitated when the solution of any of them is mixed with the solution of any of the earthy muriates, nitrates, or acetates. The solutions of the urates cause precipitations in the solutions of the metallic salts, those of gold excepted, the precipitate consisting of the metallic oxide in combination with the uric acid. The urate of iron prepared in this way, is of a reddish colour; that of copper a yellowish green; all the others are pale.

Though the neutral urates are of sparing solubility, they are much more soluble with an excess of base; hence, when boiled in solutions of these bases, or in water with the addition of them, they are dissolved in considerable quantity. An ounce, for example, of solution of potassa, the specific gravity of which is 1108, dissolves more than 60 grains of the acid. The solutions of these sub-urates are precipitated by all the acids; if a weak acid is employed in the experiment, as the prussic or carbonic, or if a small quantity only be added when a stronger acid is used, the precipitate consists of the neutral urate; and the pure uric acid is never thrown down unless by a strong acid suddenly added.

The following table is given by Dr Henry of the order of affinities of uric acid.

URIC ACID.

Barytes.
Strontites.
Potassa.
Soda.
Lime.
Ammonia.
Magnesia.
Argil.
Metallic oxides.

Uric acid is decomposed by the action of the more powerful mineral acids. Nitric acid presents with it a singular result, which serves even to form the character by which this acid can be most easily distinguished. Scheele observed, that calculi composed of it, dissolved in this acid, formed a liquor which stained the skin of a deep red colour; and this solution, if neutral, assumed by evaporation a blood red colour, which, however, disappeared on adding a single drop of nitrous acid. The same fact was observed by Bergman in his experiments; he found the deep colour assumed whenever the liquor was evaporated so far as to contain little nitric acid, and when the evaporation is carried to dryness, the colour is a very dark red; it is communicated from this dry mass to water, but is destroyed both by the acids, and by the alkalis *. Fourcroy has affirmed, that this property does not belong to the pure acid, but depends on the presence of animal matter, probably a little urée; but Dr Henry found, that it is exhibited by the acid in its purest form. By repeatedly distilling nitric acid from the uric acid, the latter is entirely decomposed; nitric oxide gas is disengaged, a portion of oxalic acid, according to Fourcroy, is formed. Dr Pearson, who has examined this operation minutely, found, that carbonic acid gas, with nitrogen gas, were disengaged during the ebullition, a strong smell of prussic acid arose, and the residual fluid deposited crystals, which he found to be nitrate of ammonia; the nitric acid, therefore, as he has explained the rationale of the process, had, by parting with oxygen to the carbon of the uric acid, formed carbonic acid; the carbon being thus abstracted, its hydrogen and nitrogen had combined and formed ammonia, with which the redundant nitric acid had united †.

Sulphuric acid heated strongly on uric acid likewise decomposes it: sulphurous acid is evolved, as Scheele found, and there is a charred residuum. Muriatic acid has little

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* Scheele's Chemical Essays, p. 200. 211.

† Philosophical Transactions, 1798, p. 30.

effect upon it; but oxymuriatic acid gas acts on it with energy, and causes its entire decomposition. When the uric acid is put into a bottle with water, and a stream of oxymuriatic acid gas is transmitted through the water, after some hours, a perfect solution is obtained. On adding to a portion of this a little lime, ammonia was disengaged, and, by evaporation of the other portion, muriate of ammonia was obtained. In this, therefore, as in the decomposition by the nitric acid, the carbon of the uric acid had been abstracted by the oxygen of the decomposing acid, and its hydrogen and nitrogen had combined and formed ammonia. The decomposition, however, as described by Fourcroy, gives results more complicated; not only ammonia and carbonic acid, but likewise malic and oxalic acids, being formed.

Uric acid is decomposed by heat: the products of the decomposition, as afforded by the acid existing in those urinary calculi which are principally composed of it, have been often examined by chemists, particularly by Scheele, Higgins, Austin, Pearson, and Fourcroy. They are water in small quantity, carbonate of ammonia, carbonic acid and carburetted hydrogen gases, prussic acid, and a matter which sublimes and condenses in a concrete form. The proportion of water is small; scarcely any sensible quantity of oil is formed; the proportion of prussic acid appears, from Austin's experiments, to be very considerable *; and there remains a considerable quantity of charcoal, which, when burnt, affords little saline matter. From these products, as well as from those which are af-

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* Treatise on Stone in the Bladder, p. 101.

forded by its decomposition by the acids, uric acid may be inferred to be a compound of carbon, hydrogen, nitrogen, and oxygen. The proportions of these have not been at all determined.

The peculiar sublimed matter obtained in this decomposition has always attracted the attention of chemists, since it was first observed by Scheele. He found, that though at first brownish, it became white by a new sublimation: it had no smell, but a sourish taste, and was easily soluble in boiling water; it was also soluble, though more sparingly, in alkohol: its solution did not precipitate lime-water. From these properties, he observed, it seemed to agree in some respects with succinic acid, while, at the same time, he appears to have supposed, that it entered into the composition of the calculus; urinary calculus, he says, "being neither calcareous nor gypseous, but consisting of an oily, dry, volatile acid, united with some gelatinous matter *." Hence, some chemists regarded this sublimate as the pure lithic acid. It is obviously different from the uric acid which exists in calculi, and which is obtained from them by solution in an alkali and precipitation by an acid; particularly in its sour taste, its much greater solubility in water, and its being capable of being volatilized by a moderate heat without decomposition. Neither is it acted on in the same manner by acids, and, in particular, it does not give a red colour with nitric acid.

Experiments were made on this substance by Dr Austin. He found, that it was decomposed by heat, affording

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* Chemical Essays, p. 204.

ammonia, prussic acid, and nitrogen gas: a portion also sublimed, which, when again submitted to the same experiment, gave the same products, and this apparently without limitation, until its decomposition was complete. Acted on by nitric acid, carbonic acid and nitrogen gases were disengaged; and the residual matter, urged with a strong fire, still gave ammonia and prussic acid *.

Some years afterwards, it was examined by Dr Pearson. He found, that it reddened the infusion of litmus, though its taste, instead of being sour, was only sharp and bitter: ten grains of it being dissolved in four ounces of boiling water, this solution, by evaporation to half an ounce, gave a copious deposite of white spicula: it was not soluble by boiling either in muriatic or nitric acid, and with the latter, it left red-coloured matter, on the acid being evaporated from it. Sulphuric acid dissolved it, with the assistance of heat, and afforded a solution from which nothing was precipitated by pure soda. Obtained from another urinary concretion, it dissolved in muriatic acid, and remained, after evaporation of the acid, in the same state as before. It was also dissolved, by boiling, by a solution of carbonate of soda, as well as by pure soda. Under the flame of the blowpipe, this sublimed matter melted, and then evaporated without any smell, leaving a slight black mark †. From the properties of this substance, Dr Pearson observes, that it appears to be analogous to benzoic acid; but the analogy is evidently very imperfect.

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* Treatise on the Stone in the Bladder, p. 115.

† Philosophical Transactions, 1798, p. 34.

Lastly, some observations have been made with regard to it by Dr Henry, which throw some light on its nature. He found it to be of a yellow colour: it impressed on the tongue a bitter taste, with a sense of coolness, but without any acrimony. Its odour is empyreumatic: it is quickly dissolved by water at any temperature, and also, though more sparingly, by alkohol. It unites easily with the pure alkalis, and from these solutions it is not precipitated by acids. It is volatile, and by repeated sublimation becomes rather whiter. Its watery solution reddens infusion of litmus; but its acid power is so weak, that a drop or two of ammonia prevents this; nor does it effervesce with the alkaline carbonates. Its watery solution, by evaporation, affords crystals, the form of which can scarcely be defined, from a portion of oily matter adhering to them, from which they can scarcely be freed. These crystals, exposed to the air, suffer no change. Pure potassa being added to them, vapours of ammonia exhale. Heated with nitric acid, they give no red-coloured matter. Their solution does not cause any precipitation from the earthy salts, as the solutions of the urates do; neither does it decompose the salts of copper, iron, gold, platina, or tin: from the nitrates of silver and of quicksilver, and from the acetate of lead, it throws down white precipitates, which are again dissolved by nitric acid. These experiments prove, as Dr Henry has observed, that the acid existing in this sublimate is neither uric, succinic, nor benzoic acid; and it appears to be different from any known acid *. It is contained in the sublimed matter

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* Dissertatio Inauguralis, p. 26.

combined with ammonia: from the products of its decomposition, it appears to be composed of the same elements as uric acid; and it is probably formed from new combinations of these elements in the process by which it is obtained.

From the preceding history of urine, it appears, that its composition is very complicated, that it contains a number of ingredients, and that these are often diversified. In the summary of its analysis by Fourcroy and Vauquelin, eleven substances are enumerated as constantly present in it, though variable in their proportions,—muriate of soda, muriate of potassa, and muriate of ammonia; super-phosphate of lime, phosphate of magnesia, phosphate of soda, and phosphate of ammonia; uric acid and benzoic acid; a gelatinous or albuminous matter; and, lastly, urée. Other principles that have been announced as existing in it are problematical, except in so far as they are the results of morbid secretion, or of the decomposition to which the urine is spontaneously liable. By this decomposition, it has been already stated, various new products are formed; acetic and carbonic acids are in particular produced, and the proportion of ammonia is much augmented; and by these the existing combinations in the urine are considerably modified: Instead of free uric and benzoic acids, it contains urate and benzoate of ammonia; the excess of phosphoric acid is saturated; and triple compounds of phosphoric acid, ammonia, and magnesia, and phosphoric acid, ammonia, and soda, are established; and acetate and carbonate of ammonia are formed.

There can be no doubt, too, but that the composition of this fluid is singularly diversified by morbid states of the system. This, though long a subject of attention to physicians, has, however, been so rather empirically; and hence our knowledge with regard to it is little advanced. The researches a few years ago of Rollo and Cruickshank threw considerable light on it; and several facts have been added by other physiologists. In the disease named Diabetes, saccharine matter is secreted by the kidneys, and often in very large quantity; and from the experiments of Cruickshank, it appears, that it is possessed of all the properties of vegetable sugar, while the proportions both of the saline ingredients and of the urée are much diminished. In dropsy, albumen is often contained in it in such a quantity, that it bears a resemblance to the serum of the blood, and is coagulated both by acids and by heat. In the dropsy, however, from diseased liver, it does not coagulate, but deposites a considerable quantity of a pink-coloured sediment, which Cruickshank found, on examination, to consist of phosphate of lime, some animal matter, to which its red colour was probably owing, and a little uric acid. In fever, particularly at the crisis or abatement of the disease, a lateritious sediment is deposited in general very copiously, and the nitrous acid, when added before the deposition takes place, gives a deep red tinge. In gout, the termination of the paroxysm is indicated by a copious deposition of a similar sediment. This sediment, adds Mr Cruickshank, from whom these facts are taken, we have generally found to be composed of lithic acid, phosphate of lime, and some peculiar animal matter, but little soluble in water; and of these, the acid generally constitutes by far the smallest part *. In those spasmodic affections that attend some nervous diseases, the urine is generally transparent, abounding in saline, and having scarcely any extractive matter; and similar appearances have been observed to precede delirium in fever. This state is discovered, by the infusion of oak bark giving scarcely any precipitate with the urine, while acetate of lead produces a very copious one. At the commencement of the paroxysm of gout, the urine, according to Berthollet, has a less proportion of acid than usual, while, towards its termination, it is even increased. In rickets, according to Bonhomme, the urine is loaded with a large proportion of phosphate of lime, derived, probably, by absorption from the bones. In other diseases, the urine exhibits other appearances: sometimes it is viscid, sometimes white and milky; sometimes, again, of a dark colour, and extremely fœtid. These, and other states in which it occurs, have not hitherto been accurately chemically examined, though undoubtedly, in a medical point of view, they must afford important results.

It appears, too, that in different animals the urine varies considerably. In that of gramnivorous animals, the uric acid is altogether wanting, while the benzoic is generally

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* Proust has affirmed, that this sediment consists chiefly of a peculiar acid, which, from its colour, he has named Rosacic Acid, and which, he adds, is distinguished from uric acid, by its greater solubility in hot water, by its not crystallizing so easily, and by giving a violet precipitate with muriate of gold *. We have no farther information with regard to it, and it therefore requires more investigation.

* Annales de Chimie, tom. xxxvi. p. 258.

present in large proportion. Rouelle had examined that of the horse; he found it to afford no phosphorus: it contained sulphate and muriate of potassa in considerable quantity, carbonate and sulphate of lime, with the peculiar saponaceous extract, or urée, and a matter which rendered it viscid: and these results have been, in general, confirmed by the recent analysis of it, by Fourcroy and Vauquelin *; its ingredients, as determined by this analysis, being carbonates of lime and soda, muriates of potassa and soda, benzoate of soda, and urée. That of the cow, according to Rouelle's analysis of it, gives results nearly the same, all its salts having a base of potassa. That of the camel he found to contain carbonate, sulphate, and muriate of potassa, with urée.

THE Concretions which sometimes form in the kidneys or bladder, being derived from the urine, fall properly to be considered under its chemical history. The investigation of their nature and properties, is of much importance, at least in a medical point of view, as they give rise to one of the most painful diseases to which man is subject, and it is only by chemical researches that we can hope to discover the causes of their production, and of course the means by which this may be counteracted, or even by which, when they have been formed, they may be dissolved. We have now, therefore, to deliver the chemical history of URINARY CALCULI.

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* Mémoires de l'Instit. National. tom. ii. p. 431.

Though these concretions had long been attended to by the chemists, nothing in reality was known with regard to them, previous to the discovery of the uric acid by Scheele. From this discovery, it appeared to form the basis of these concretions, and from that time the knowledge of this fact regulated all the investigations on this subject. Bergman confirmed the discovery of Scheele. Experiments continued to be repeated and diversified on these concretions, and on their solvents : it was discovered, that there existed others besides those composed of uric acid ; and within these few years, our knowledge of them has been much extended, by the researches of Pearson, Wollaston, and Fourcroy and Vauquelin. Dr Wollaston, in particular, determined the composition of other three species of these concretions, besides that composed principally of the uric acid ; and in the analysis by which these important distinctions were established, discovered the existence of various principles in urinary calculi, which it had not been before known that they contained *. And Fourcroy and Vauquelin, by an extensive series of experiments, established similar results †, and have described, with considerable minuteness, the diversified appearances these concretions present, either from chemical composition or mechanical structure. The result of all these researches

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* Philosophical Transactions, 1797.

† { Mémoires de l'Institut. National. tom. ii. p. 112.
{ Annales du Museum National. tom. i. p. 93.

It is but justice to remark, that Dr Wollaston's dissertation was published in the Philosophical Transactions two years before the memoir of Fourcroy and Vauquelin was read before the French National Institute ; and although the experiments is, that the following substances enter more or less abundantly into the composition of urinary calculi: uric acid, urate of ammonia, phosphate of lime, phosphate of ammonia and magnesia, oxalate of lime, silex, and animal albumen, these principles being more or less common, and in greater or less proportion, giving rise to numerous varieties. Hence there is considerable difficulty in adopting an arrangement with regard to them, and this requires some observations, before proceeding to their individual history.

The calculi which are by far the most common, are those composed principally of uric acid. They are generally of a brown or yellowish colour, smooth on the surface, and with a texture compact or radiated; they are perfectly soluble in alkaline solutions, and give a red colour when treated with nitric acid.

A calculus had been observed, different in its properties from the former, particularly in fusing by the heat of the blow-pipe, into an opaque white glass, instead of being decomposed. This Dr Wollaston found to be composed principally of phosphate of magnesia and ammonia.

Another had been distinguished by surgeons by the name of the Mulberry Calculus, from its dark colour and irregularly knotted surface, bearing some resemblance to that fruit; and it had also been observed, that this was

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of Pearson, published in the Philosophical Transactions the year after Wollaston's, are referred to in that memoir, no notice is taken of those of the latter chemist; yet they anticipate nearly every thing which the French chemists have announced as their own discoveries.

little affected by an alkaline solution. Dr Wollaston found it to be composed of oxalate and phosphate of lime.

He lastly discovered one consisting entirely of phosphate of lime, of a pale brown colour, so smooth as to appear polished, and in its texture very regularly laminated or composed of concentric crusts, and soluble, though slowly, in nitric or muriatic acid.

These form four species, under which Dr Wollaston has arranged urinary calculi: 1st, The uric acid concretion: 2d, The fusible calculus or phosphate of ammonia and magnesia: 3d, The mulberry calculus, or oxalate and phosphate of lime; and, 4th, What he named the Bone Earth Calculus, as composed of phosphate of lime, which forms the basis of bone.

The arrangement of urinary concretions by Fourcroy and Vauquelin, is much more minute and complicated. They observe, that in all of them there exists a quantity of animal matter which appears to connect their particles; but, independent of this, which is common to the whole, they may be arranged under three classes; the first consisting of calculi formed of a single substance; the second composed of two substances; and the third containing more than two substances, frequently even four. Under these three classes might be placed, it is evident, numerous combinations; but, confining themselves to those which they had actually observed, they have formed twelve species; three belonging to the first division, seven to the second, and two to the third.

The following Table presents a view of this arrangement.

GENUS I. Composed of one ingredient.	*Species* 1.	Calculus of uric acid.
	—— 2.	——— of urate of ammonia.
	—— 3.	——— of oxalate of lime.
GENUS II. Composed of two ingredients.	—— 4.	——— of uric acid and earthy phosphates in distinct layers.
	—— 5.	——— of uric acid and earthy phosphates intimately mixed
	—— 6.	——— of urate of ammonia and phosphates in distinct layers.
	—— 7.	——— of urate of ammonia and phosphates intimately mixed.
	—— 8.	——— of earthy phosphates, either mixed intimately, or in fine layers.
	—— 9.	——— of oxalate of lime and uric acid in distinct layers.
	—— 10.	——— of oxalate of lime and earthy phosphates in distinct layers.
GENUS III. Composed of three or four ingredients.	—— 11.	——— of uric acid, or urate of ammonia, earthy phosphates, and oxalate of lime.
	—— 12.	——— of uric acid, urate of ammonia, earthy phosphates, and silex.

It is sufficiently evident, that this arrangement is not strictly chemical, since a number of the species are founded, not on differences in composition, but on differences in mechanical structure. And if the classification of calculi were to be established on this principle, there is every probability that the species would be much more numerous than those Fourcroy and Vauquelin have established; for varieties in structure, or in the layers of which the concretion consists, must arise from very slight causes, and may be almost indefinitely diversified. Hence, even under a practical point of view, the utility of minute distinctions from this source must be doubtful.

The classification of Wollaston is more precise, but, perhaps, it is rather too simple: And, indeed, he did not give it as a systematic arrangement of calculi, but merely pointed out those which he had examined, and found different from the common uric calculus. Yet, the four species which he has enumerated, are sufficiently well defined. If any addition can be made to them, in the present state of our knowledge, it is that of the urate of ammonia, described by the French chemists, and which, as of determinate composition, must be regarded as a species. Under these may be placed those calculi in which these ingredients are intimately combined, classing them according to the predominating ingredient. And, after these, may be placed the mechanical aggregates of these species, at least those of them which, from their frequent occurrence, seem to demand some notice.

Species 1. Uric Acid Calculus. This is by far the most common of the urinary concretions. All that Scheele had examined appear to have been of this kind. Dr Pearson has remarked, that of 200 specimens which he had analysed, not more that six did not contain uric acid, though he found its proportion very various. And Fourcroy and Vauquelin found among 600 calculi, more than 150 composed of pure uric acid. Calculi of this kind are usually in fine and close layers, fibrous or radiated, smooth on the surface, though sometimes a little rough, of a yellowish or brown colour, similar to that of wood, of various shades; their form is spheroidal, compressed, or elongated; their size very various. They are rather brittle, and have a specific gravity, varying from 1.276 to 1.786, but usually above 1.500. They blacken without melting on burning fuel; exhale an odour similar to that of bone burning, and give, by distillation, ammonia and prussic acid. They are insoluble in cold water, but when in powder, and the water is at the temperature of 212°, a perfect solution is obtained, and small crystals are deposited on cooling. They are soluble in the cold in a solution of pure potassa or soda, and from the solution a precipitate of a fine white powder is thrown down by the acids. Lime-water likewise dissolves them, but more sparingly. In solutions of the alkaline carbonates, they remain, according to Scheele, unchanged: according to the experiments of Dr Egan, however, they are dissolved even by weak solutions, and also when the alkali is super-saturated by carbonic acid *. The weaker acids have no effect on them. Even the muriatic does not dissolve them. Nitric acid, however, assisted by heat, acts upon them, and, as has been already remarked, produces the deep red colour which is so characteristic of uric acid. In many of them the uric acid appears to be nearly pure: thus Scheele, in those he examined, could not discover a trace of lime; in others, however, there is an intermix-

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* Transactions of the Irish Academy; or Philosophical Magazine, vol. xxiii. and xxiv.

ture of other ingredients, particularly of phosphate of lime, and phosphate of magnesia and ammonia.

Species 2. Calculus of Urate of Ammonia. This is acknowledged by Fourcroy and Vauquelin to be one of the rarest of the urinary concretions, yet they found it sometimes to occur, and as it is of determinate composition, it is necessary to admit it as a species. The calculus formed of it has some resemblance in structure to the preceding, or consists of layers less sensibly striated, however, than those of the pure uric acid : its colour is also lighter, and often inclining to grey, or greyish white. Their form is the same, their surface smooth, sometimes brilliant and crystalline, and sometimes the external layer is pure uric acid ; they have almost always, too, a nucleus of matter different from the body of the calculus. Their specific gravity is from 1.225 to 1.720. With regard to chemical characters, they are well distinguished by their solubility in alkaline solutions, and their giving out, while they dissolve, a strong ammoniacal odour, two characters which are not found together in any other species. They are also soluble alone in hot water, and are rendered still more soluble by an excess of ammonia. All the acids abstract their base, and reduce them to the state of uric acid. Heated by the blow-pipe, they immediately exhale ammonia, and then present the same appearances as the preceding species.

Species 3. Calculus of Phosphate of Magnesia and Ammonia. This is the fusible calculus of Wollaston. It is to be remarked, however, that it scarcely ever forms a calculus alone: it is either, if pure, discharged in the form of a white sand, which consists of very minute crystals, er, when it composes a concretion, it is either intermixed with other ingredients, particularly with uric acid and phosphate of lime, or it forms layers more or less fine, which alternate with layers of these, or cover a nucleus of uric acid. It is well distinguished when in these layers, or when it is predominant in a mixed calculus, by its lamellated sparthose structure, its white colour, and the closeness and fineness of its texture; it is soft and smooth to the touch, is easily sawed through, and gives a fine light powder of a brilliant whiteness. It has a taste mild and sweetish, without feeling dry like phosphate of lime. With regard to chemical characters, it is distinguished by melting before the flame of the blow-pipe into a white enamel; placed on burning fuel, it blackens and exhales an empyreumatic ammoniacal odour, and melts when the heat is raised. It dissolves in water sparingly, still, however, so far, that when the water is boiled on it and evaporated, it deposites minute crystals on cooling. It dissolves easily in the acids, even those that are weak; and when a calculus composed of it is immersed in dilute muriatic acid, or water impregnated with carbonic acid, the phosphate of lime and magnesia is dissolved; and there remains a membranous matter in light flakes, consisting of the albumen mixed with it. The fixed alkalis disengage its ammonia, combine with its acid, and separate the magnesia. Ammonia has little effect on it. By subjecting calculi, into the composition of which it enters, to the successive action of these re-agents, they may be analysed. Thus, according to Dr Wollaston's method, the phosphate of lime and ammonia is dissolved by distilled vinegar in the cold, with scarcely any phosphate of lime.

Muriatic acid poured on the residuum dissolves the phosphate of lime. And, lastly, a fixed alkaline solution takes up the uric acid.

Species 4. Calculus of Phosphate of Lime. From the observations of Dr Wollaston, it appears, that this substance sometimes composes the entire calculus, though more generally it is usually mixed with other ingredients, particularly with uric acid, and with phosphate of magnesia and ammonia. In the first case, the calculus is described as being of a pale brown colour, and so smooth as to appear polished; when sawed through, it is found very regularly laminated, and the laminæ, in general, adhere so slightly to each other, as to separate with ease into concentric crusts. It dissolves entirely, though slowly, in muriatic or nitric acid. Exposed to the flame of the blow-pipe, it is first slightly charred, but soon becomes perfectly white, retaining its form, until urged with the utmost heat from a common blow-pipe, when it may be completely fused. It appears to be more fusible than the phosphate of lime, which forms the basis of bone, which Dr Wollaston supposes owing to the latter containing a larger proportion of lime*. The calculi of which phosphate of lime is the basis, but in which there are also other ingredients, particularly phosphate of magnesia and ammonia, and uric acid, are more numerous, and are diversified in the appearances they present. According to the observations of Fourcroy and Vauquelin, it appears in these either under the form of layers, friable, or having little hardness, breaking into scales under the saw, of a greyish white colour, dull, and without any lamellated or spathose crystalline form, or, instead of layers, it presents incoherent grains, friable, and with little induration; and, by this dry and earthy appearance, and the dulness of its colour, it is distinguished from the phosphate of magnesia and ammonia. Calculi of either kind are charred by being heated, from the animal matter they contain; calcined to whiteness they do not afford lime. They are dissolved by the acids even when much diluted, and the phosphate of lime is again precipitated by the alkalis; they are not affected by alkaline solutions. From their state of intermixture, however, they are liable to variations both in their physical properties and chemical characters. Their colour is often shaded or veined; their texture is even not uniform, crystalline grains of the phosphate of magnesia and ammonia being intermixed through it; when the two phosphates merely are intermixed, the colour is pure white, and their cohesion generally inconsiderable; when the uric acid is present the colour is darker, and they have more hardness. And, in all these, the different ingredients can only be recognised with certainty by analysis.

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* Philosophical Transactions, 1797, p. 395.

Species 5. Calculus of Oxalate of Lime. This species forms what has been long known by the name of the Mulberry Calculus, from its colour and its rough pointed surface: the composition of it was discovered by Wollaston. It is usually of a dark brown colour externally, frequently grey within: its surface is usually uneven, presenting tubercles more or less prominent, frequently rounded, sometimes pointed, and either rough or polished: it is very hard, difficult to saw, and appears to consist of successive unequal layers: it is also the heaviest of the urinary concretions. With regard to chemical characters, it is less affected by the application of the usual re-agents than any other calculus. The pure alkaline solutions have no effect upon it, and the acids dissolve it with great difficulty. When it is reduced, however, to fine powder, both muriatic and nitric acid dissolve it slowly. The solutions of the alkaline carbonates decompose it, as Fourcroy and Vauquelin have observed; and this affords us the easiest method of analysing it: the calculus in powder being digested in the solution, carbonate of lime is soon formed, which remains insoluble, and is easily distinguished by the effervescence produced by the addition of weak acetic acid, while there is obtained in solution the compound of oxalic acid with the alkali of the alkaline carbonate: from this the oxalic acid may be precipitated by acetate of lead or of barytes; and this oxalate thus formed may be afterwards decomposed by sulphuric acid. Another method of analysing this calculus is by exposure to heat: its acid is decomposed, and by raising the heat sufficiently, pure lime is obtained, amounting to about a third of the weight of the calculus. This species, it is remarked by Fourcroy and Vauquelin, contains more animal matter than any other, from which its colour appears to be derived, and which gives to it also its hardness and dense aggregation: this animal matter appeared to them to be a mixture of albumen and urée.

Fourcroy and Vauquelin found in two calculi of the six hundred which they analysed, siliceous earth: it was mixed with uric acid and urate of ammonia, in the nucleus and internal layers.

There is also present in all these calculi, as has been already remarked, a portion of animal matter, which has perhaps been hitherto too little attended to: it is it, according to Fourcroy and Vauquelin, which is the source of the colour, induration, and texture of a number of these concretions; and it appears to have an important share in their formation: it is found even in those which appear most white and crystalline, and in others is contained in much larger quantity: it often remains in flocculi when the other ingredients have been dissolved by re-agents: these chemists have supposed it to be analogous to albumen or gelatin, with the exception of that in the mulberry calculus, which appears to approach to urée.

Such are the ingredients in urinary calculi, and the species under which they may be arranged. It is only farther to be remarked, that they are still more diversified by mechanical intermixture, layers of these ingredients alternating, and forming a concretion. As such intermixtures must be in a great measure accidental, they can scarcely be arranged with any precision. Those which have been most frequently observed, and which are particularly pointed out by Fourcroy and Vauquelin, are, 1st, The mixture of uric acid and of earthy phosphates; the former generally forming the nucleus, and the phosphate of lime and phosphate of magnesia and ammonia being either intermixed or in alternate layers; 2dly, Those of urate of ammonia and earthy phosphates, the nucleus of this being commonly the urate of ammonia, and the layers being the phosphate of lime and phosphate of magnesia and ammonia mixed with it, and, at the same time, sometimes alternating with fine layers of it, or even of uric acid; 3dly, That of oxalate of lime and of uric acid, the first generally occupying the centre; 4thly, That of oxalate of lime and earthy phosphates; the first forming the nucleus, the second enveloping it in different layers; and, lastly, The alternation of uric acid alone or mixed with urate of ammonia, with oxalate of lime and earthy phosphates; the centre or nucleus being oxalate of lime, the intermediate layers uric acid or urate of ammonia, and the exterior, earthy phosphates more or less intermixed with each other and with uric acid. A farther examination will no doubt give many more varieties of these mechanical mixtures; since, when a concretion is once formed, it appears to serve as a nucleus to other formations, which must be liable to be modified and interrupted according to the diet, the state of the system, and of the secreting organ.

Fourcroy and Vauquelin have given a very good summary of the chemical phenomena presented by re-agents on the usual ingredients of urinary calculi, and by which these may be recognised, and the composition of the concretion inferred. In applying a pure alkaline solution, the re-agent by which the analysis is generally first attempted, five appearances present themselves, from which such indications may be drawn. 1st, The alkali may dissolve the calculus entirely, and without causing any evolution of ammonia; in which case it may be inferred, that it has consisted of pure uric acid; 2dly, The solution may be equally complete as in the first case, but accompanied with a strong ammoniacal odour: the calculus has then consisted of urate of ammonia, without any earthy phosphate; 3dly, The alkali may dissolve only a part of the calculus in powder, without causing any exhalation of ammoniacal odour; and in this case, which is rare, there is indicated a mixture of uric acid and phosphate of lime, which the solution separates; 4thly, The alkaline ley, in effecting a similar partial solution, may at the same time disengage ammonia; and in this case, much more common, there are indicated the presence of uric acid which has been dissolved, and of phosphate of magnesia and ammonia which has been decomposed; hence the undissolved portion must contain the magnesia, which may be discovered by weak acetic acid, and the addition of potassa to the solution it effects; while the alkaline ley contains the phosphoric acid, which may be precipitated by lime-water, and the uric acid, which may be thrown down in a crystalline form by muriatic acid; 5thly, There is presented sometimes, in the treatment of the calculus by the alkaline ley, another appearance,—that of an evolution of ammonia, while no uric acid can be precipitated from the solution by the addition of the other acids; indicating of course the presence only of phosphate of magnesia and ammonia, mixed generally with more or less phosphate of lime. The oxalate of lime is not at all dissolved by the alkaline solution, but by the alkaline carbonates producing at the same time carbonate of lime, by which it may be recognised, as well as by furnishing lime, when the calculus has been urged with a strong heat*.

The investigation of the composition of urinary concretions leads to the interesting question, how far their solution in the bladder may be practicable, and by what agents this, if it can be accomplished, will be best performed. It is sufficiently evident, that being of very different chemical composition, the same solvent cannot be applicable to all of them; yet still there may be a possibility of solvents being introduced adapted to each.

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* Mémoires de l'Instit. National. tom. iv. p. 125. 130. 137.

Long experience has sufficiently established the advantage derived in calculous affections from the use of alkaline remedies; and as the calculi composed of uric acid are those which are by far the most abundant, it is no doubt, from the chemical action they exert upon it, that the benefit is derived. Where the pure alkali is used, a real solvent power may be exerted; and it has been proved, that the alkali is secreted by the kidneys, so as to render the urine sensibly alkaline, and even capable of acting on the calculus out of the body. Yet the solvent power is very inconsiderable, and the remedy, at the same time, proves so irritating, when taken to any considerable extent, that the solution of a calculus even of small size can perhaps be scarcely expected. The pain and irritation which attend the disease, however, are considerably alleviated by their habitual use, and this even when the alkali is saturated or super-saturated with carbonic acid,—a circumstance with regard to which there appears some difficulty in giving an explanation, since the alkalis in this state have been supposed not to act on uric acid. From the experiments of Dr Egan, already stated, this, however, appears to be a mistake; though the relief obtained from the use of these may also be in part derived from the saturation of the phosphoric acid which is likewise secreted; the urine is thus rendered less irritating, and the tendency to a deposition of uric acid diminished, all acids hastening the precipitation of this acid from urine. Lime, under the form of lime-water, has also been employed as a solvent; but its use has seldom been general, either from the prejudice that it itself entered into the composition of these concretions, and would therefore rather favour their formation; or from the supposition, that, on account of its sparing solubility, so little of it could be introduced into the system, that it would have no great power. The experiments of Dr Egan, however, have shown, that lime-water acts with more energy than an alkaline solution of similar strength, in destroying the aggregation of a urinary concretion; and I observed this effect strikingly displayed in a comparative trial which these experiments led me to make. In a dilute solution of pure potassa, a calculus of the uric acid kind was in part dissolved, the liquor, after a short time, giving a copious white precipitate with muriatic acid; but the remaining calculus preserved its aggregation, apparently without much alteration, the external layer having been merely removed; while a calculus of a similar kind, and discharged from the same person, immersed in lime-water, became in a few days white and spongy: it appeared at length to be entirely penetrated: its cohesion was subverted: it presented a kind of loose scaly appearance, and the least touch made it fall down. The lime probably operates more upon the albumen or animal matter, which appears to serve as the cement or connecting substance, than upon the uric acid; and in endeavouring to discover solvents for these concretions, our views ought perhaps rather to be directed to this operation than to the effect on the saline matter. If lime, when received into the stomach under the form of lime-water, can be secreted by the kidneys, as the alkalis unquestionably are, it would appear, from these observations, to be superior to them as a solvent. And Dr Egan likewise found it to be effectual in preventing the deposition of uric acid from urine.

Those calculi which are composed of oxalate of lime, phosphate of lime, or phosphate of magnesia and ammonia, not being soluble in alkalis, it has been supposed that the use of alkaline remedies can be attended with advantage only where the calculus consists principally of uric acid, and that the solution of the others, were it attempted, must be by the action of weak acids. If the view now given, however, be just, the use of the alkalis, or of lime-water, may be useful, even in these cases, by acting on the animal matter; and it appears very doubtful, if acids can ever be given to that extent to render the urine sufficiently powerful from their operation to exert any solvent power.

Fourcroy and Vauquelin have proposed *, that the solution of urinary concretions should be attempted by the injection of the proper solvents into the bladder; the uric acid calculus being dissolved, they observe, by some days immersion in an alkaline ley, so weak that it might, as they suppose, be safely injected, and the calculi of the phosphates being dissolved by water, in which there was so little muriatic acid as to give only a slight sourness. From the extreme irritability of the bladder, however, with regard to every fluid but that which

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* Mémoires de l'Institut. National. tom. iv. p. 147.
Fourcroy's System, vol. x. p. 351.

it usually contains, and to which the state of that irritability is adapted, there can be little doubt but that this project is altogether impracticable.

The preceding history of urinary concretions apply to those formed in the human system. They are also sometimes found in other animals; and calculi of this kind from the dog, the horse, the hog, and the ox, have been examined *. They have presented the singularity, that the uric. acid is altogether wanting, these concretions consisting of phosphate or of carbonate of lime with animal matter.

SECT. VII.

SYNOVIA.

THIS name is given to the liquor which is found within the capsular ligaments of the joints, and which is designed to facilitate the motion of the articulated bones. It was submitted to chemical examination by Margueron, from whose memoir † the following concise account of it is taken.

It is a fluid extremely viscous, more or less transparent, and of a greenish colour: when it is withdrawn

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* Pearson, Philosophical Transactions, 1798, p. 39.
Fourcroy, Annales du Museum National. tom. iii. p. 304.
tom. iv. p. 329.

† Annales de Chimie, tom. xiv. p. 123.

from its capsule, it becomes gelatinous; but after standing for some time, it loses this, and deposites a fibrous elastic matter. It mixes easily with cold water by agitation, and renders it viscous: when the mixed liquid is heated, it becomes milky, and some pellicles are formed, but the liquor remains viscous as before.

Acids added to synovia, produce a flocculent precipitate, which is, however, soon redissolved, nor is the viscosity lessened. When the stronger acids are diluted with from 12 to 15 parts of water, they still render this liquor turbid, without impairing its viscid consistence; but when very much diluted, so that the acidity is scarcely perceptible, this consistence disappears, the liquor becomes clear and transparent, and there separates from it a fibrous-like matter. These phenomena were, in particular, produced by the action of acetous acid. The liquor remaining after this precipitation being heated, affords albuminous pellicles, and when these are withdrawn, it gives, on evaporation, crystals of muriate and of acetate of soda. From 288 parts of synovia, there were separated by the action of acetic acid, 34 of the fibrous-like matter, and afterwards, by heat and evaporation, 13 of albumen, 5 of muriate of soda, and 3 of acetate of soda.

The fibrous matter which is thrown down in these experiments, is not perfectly similar in its properties to any known animal principle; for although it has some resemblance, both to albumen and to fibrin, it still differs from both. Margueron observes, that it resembles fibrin, or rather the gluten of wheat, with which he compares it, in colour, taste, and odour, in elasticity and tenacity; but it differs in being soluble by agitation in cold water, and in being precipitated in flakes by acids and alkohol. He concludes, perhaps without much precision, that it is albumen in a particular state.

Alkohol separates albumen from the synovia, but not the peculiar fibrous matter, and hence the viscidity is not impaired, but it immediately disappears on adding acetic acid, and a portion of fibrous matter is deposited.

Synovia affords precipitates with lime water, and with the solutions of barytes, strontites, potassa, and even ammonia, consisting principally of the phosphate of lime it contains; and from the presence of the same substance, it gives a precipitate with oxalic acid. The alkalis at the same time render it more fluid, and even dissolve it when it has been inspissated from exposure to the air.

Exposed to a moist atmosphere, it passes into a state of putrefaction, and exhales ammonia. Decomposed by heat, it affords empyreumatic oil and carbonate of ammonia; and the residuum contains muriate and carbonate of soda. Phosphate of lime is obtained from the incineration of its charcoal.

Margueron concludes, as the result of his analysis of this fluid, that it is composed of fibrous matter 11.8, albumen 4.5, muriate of soda 1.75, carbonate of soda 7, phosphate of lime 7, the remaining quantity to make up 100 parts being water.

ARTHRITIC CONCRETIONS, or those deposited sometimes during a paroxysm of gout in the joints, are probably formed from this fluid, or at least are deposited by its medium. They were found by Dr Wollaston to consist of urate of soda[*]; a discovery confirmed by the experiments of Fourcroy[†]. The connection of gout with gravel has always been observed; and the deposition of these concretions probably depends on some cause similar to that on which the formation of urinary calculi depends.

SECT. VIII.

AMNIOTIC FLUID.

THE fluid with which the fœtus is surrounded in the amnios, is entitled to notice, principally as having furnished what Vauquelin has regarded as a new acid. He obtained it from the amniotic liquor of the cow: this has a reddish colour, is somewhat viscid and mucilaginous, has an acid and bitter taste, and a faint odour. It reddens the more delicate vegetable colours.

When this liquid is evaporated, it is covered with a scum, in which are formed some small brilliant crystals; and by continuing the evaporation, it is reduced to a thick viscid consistence like that of honey. If this be treated with alkohol boiled on it, a quantity of viscid dark coloured matter, nearly of the consistence of pitch, remains undissolved; when the alkohol is poured off from this, on cooling, it deposites brilliant crystals, in the form of slender prisms, nearly an inch long. These crystals are the amniotic acid. They may also be obtained by reducing the liquor to one-fourth of its volume by evaporation; they are coloured by a small quantity of the animal matter, which may, however, be abstracted by washing with a little water, then dissolving and again crystallizing them..

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[*] Philosophical Transactions, 1797, p. 389.

[†] Annales du Museum National. tom. i. p. 100.

This acid, discovered and examined by Vauquelin and Buniva *, is white, brilliant; has a slightly sour taste, reddens infusion of litmus, is sparingly soluble in cold water, but more so in warm water, and crystallizes on cooling: it is also soluble in alkohol. It combines with the alkalis, and forms soluble salts, which are decomposed by the other acids, the amniotic acid being precipitated. It does not decompose the alkaline carbonates, unless when aided by heat; neither does it precipitate the earthy salts, or the nitrates of silver, quicksilver, or lead. Exposed to heat, it is decomposed, becomes black, exhales ammonia and prussic acid, and leaves a bulky charcoal. In these properties it has some points of resemblance both to saccho-lactic and to uric acid; but the former differs from it in being soluble in alkohol, and in affording neither ammonia nor prussic acid, when decomposed by heat; and the latter, equally in its insolubility in alkohol, its different crystallization, and the red colour which it receives from nitric acid.

The animal matter which exists along with this acid in the liquor of the amnios of the cow, has some peculiar characters. It is of a reddish brown colour, of a taste somewhat saline, and has a strong smell: it is readily so-

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* Annales de Chimie, tom. xxxvi. p. 265.

luble in water, to which it communicates its colour, but without any viscidity or gelatinous consistence; it is insoluble in alkohol, which even precipitates it from its watery solution. Decomposed by heat, it affords the usual products of animal matter, with a considerable quantity of prussic acid: its charcoal, when incinerated, gives phosphate of magnesia. Nitric acid disengages from it nitrogen and carbonic acid gases, without converting it into any acid. It is not precipitated by tannin.

With these two principles, there is present in this liquid a portion of sulphate of soda, which may be obtained by crystallization from the evaporated liquor, after this has deposited the amniotic acid.

It is singular, that the human amniotic fluid is altogether different in its composition. Vauquelin and Buniva could not discover in it any amniotic acid, but found it to consist of albumen, and perhaps gelatin, with a little muriate and carbonate of soda and phosphate of lime. From containing these principles, it is of a mild, saline taste, a whitish colour, and a little viscid. It becomes still more milky when heated; acids render it clear. Alkohol and also the alkalis separate albuminous flakes from it. Infusion of galls produces a copious precipitate; and a white precipitate is formed by nitrate of silver, insoluble in nitric acid, indicating the presence of muriatic acid.

SECT. IX.

HUMOURS OF THE EYE.

THE ball of the eye contains three liquids differing in their physical properties, though but little in their chemical nature: the Aqueous Humour, situated in the anterior chamber; the Crystalline Humour or Lens, occupying the central space; and the Vitreous Humour, which fills up the greater part behind the lens. Of these we had very little chemical knowledge, until their analysis was executed by Mr Chenevix; from whose dissertation *, with one or two facts from a short memoir by Nicholas †, subsequent to that of Chenevix, the following account of them is taken.

AQUEOUS HUMOUR. This is a clear transparent liquid, of the specific gravity of 10090, at 60° of Fahrenheit. When fresh, it has very little smell, or taste. It causes very little change in the vegetable re-active colours; a little ammonia, which causes it to give a green tinge, being apparently produced from decomposition.

When exposed to the air, at a moderate temperature, it evaporates slowly, and becomes slightly putrid. When made to boil, a coagulum is formed, but so small as hardly to be perceptible. Evaporated to dryness, a residuum remains, weighing not more than 8 *per cent.* of the original liquor.

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* Philosophical Transactions, 1803.

† Annales de Chimie, tom. liii.

ter, the colour is removed, and a white substance remains, having all the properties of fibrin.

When the water which has been employed in this operation is examined, it is found, besides the colouring matter derived from the blood, to contain albumen, gelatin, saline matter, and fat, the last no doubt being adventitious, the others perhaps being constituent parts of the flesh. By heating this water gradually, the albumen first coagulates and separates in flakes; if these be removed, and the liquor farther evaporated, it becomes gelatinous when cold; the fat, during the boiling, separating and collecting on the surface. By this simple analysis made by Thouvenel, the immediate principles of muscle are discovered.

Besides these, this chemist obtained a peculiar extractive matter, by evaporating the jelly to dryness, and treating it with alkohol: the gelatin and saline matter remain undissolved, and the alkohol takes up this peculiar matter, which, by evaporation, may be obtained in the solid form. It is of a brownish red colour, has a pungent, even acrid taste, and an odour somewhat aromatic: by being heated a little more than is necessary to dry it, it boils and swells, and assumes the odour and saccharine taste of caramel. It is deliquescent, and, when in solution, becomes sour from exposure to the air, passing into acetic acid, and depositing charcoal. Subjected to destructive distillation, it gives water, ammonia, and acetic acid; and its residual charcoal contains muriates of potassa and soda.

By boiling water on the muscular fibre previously washed, the saline matter it contains is dissolved, and may be detected in the gelatinous solution. Phosphates of soda and of ammonia were known to be thus procured; and, from Mr Hatchet's experiments, it appears, that phosphate and carbonate of lime are also present. They are more abundant, he found, in the muscle of beef than in that of veal; and he hence concludes, "that the earthy matter is more abundant in the coarse and rigid fibre of adult and aged animals, than in the tender fibre of those which are young; and this seems to be corroborated by the tendency to morbid ossification so frequently observed in aged individuals of the human species *." In young animals, too, the gelatin is more abundant in the muscular fibre than in those of advanced age; in the latter, the fibrin appears to predominate.

When the entire muscular flesh is boiled at once in water, its principles are more completely dissolved, except the fibrin, which is in part dissolved, but which partly also forms threads that float in the liquor. In this liquid these principles can be discovered. The gelatin and albumen are detected by the infusion of tannin; and from the presence of the gelatin, the liquor, too, is liable to become sour on keeping, acetous acid being formed. Lime-water, or ammonia, produces in it a slight precipitate of phosphate of lime: oxalic acid detects the lime; and, according to Fourcroy, nitrate of silver indicates the presence of muriatic acid. If the decoction be strained and evaporated, it becomes gelatinous; and by being boiled down sufficiently, it even becomes perfectly solid and firm, in consequence of which it can be preserved for a long time without injury. Compositions of this kind,

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* Philosophical Transactions, 1800, p. 396.

with the addition of aromatics and a little muriate of soda, form the tablets of portable soup.

The muscular fibre, in its relations to the chemical reagents, presents phenomena conformable to what we know of its immediate principles.

When exposed to the air, it soon becomes tainted, and at length putrid,—a change which, as Mr Hatchet has supposed, depends principally on the presence of gelatin; as he found, that flesh, deprived of this principle by long maceration and subsequent boiling, is little liable to this change.

When the air is excluded, and the flesh is immersed under water, it suffers a peculiar species of decomposition, in consequence of which it is converted into a fatty matter like spermaceti,—a change which is to be considered under the history of the general chemical changes to which animal matter is liable.

Exposed to heat, it affords all the usual products arising from the decomposition of animal matter. Berthollet, examining the acid which it affords, found, that it is of a peculiar nature: he named it the Zoonic; but it has since been discovered to be merely the acetic. Five hundred grains of the washed muscular fibre of beef, left, in Mr Hatchet's experiments, 108 grains of charcoal, which, by incineration, afforded 25.6 grains of earthy residuum, the greater part of which was carbonate of lime, with a small proportion of phosphate, and a little pure lime.

The acids decompose the muscular fibre, with results nearly the same as those produced by their action on fibrin. The action of nitric acid has in particular been examined, and is important. Berthollet long ago remarked, that it caused an evolution of nitrogen gas. Mr Hatchet has shown, that washed muscular fibre, acted on by nitric acid diluted with three parts of water in the cold, is converted into a substance soluble in boiling water, and analogous to gelatin; the acid, at the same time, acquiring a yellow tinge; and the residual matter consists principally of fat, with a portion of undecomposed muscular fibre. When the washed flesh was acted on by boiling nitric acid, it was dissolved; the solution was of a yellow colour, and a portion of fatty matter floated on the surface: ammonia threw down a precipitate of oxalate, with a little phosphate of lime: oxalic acid, therefore, had been formed. When the recent muscle, without any preparation, was dissolved in nitric acid, the solution, when saturated with ammonia, became of a deep orange colour: it also formed animal soap with the alkalis,—phenomena indicating the presence of albumen *.

The action of nitric acid on the muscular fibre has been more lately examined still more minutely by Fourcroy and Vauquelin; and some important results have been established, though only a very confused statement of them has hitherto been published †.

A mixture of muscular flesh, with an equal quantity of nitric acid and of water, being heated in a matrass, gave out an elastic fluid, found to consist of nine-tenths nitrogen and one-tenth carbonic acid. The residuum consisted of the remains of the flesh, still retaining in part its fibrous appearance, of a yellow liquor, and of a yellow

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* Philosophical Transactions, 1800, p. 391. 393.

† Annales de Chimie, tom. lvi. Nicholson's Journal, vol. xiii.

fatty matter, collected on the surface of the liquor. This being removed, and the liquor filtered, the residual fibrous matter was found to have the following properties: it gave to boiling water a yellow colour, and the property of reddening vegetable blues; and even after having been repeatedly washed, it continued to give colour, though no longer acidity. Washing rendered its colour deeper than at first; and when diffused in a little water, it reddened litmus-paper. Its solution in alkalis was of a blood-red colour: acids precipitated it in yellow flakes. It feels greasy and pitchy; has a rancid smell, and a bitter taste; and melts, swells, and gives an oily vapour when heated. By a farther examination, it was found to saturate alkalis, so as nearly to disguise their properties: its combinations with potassa and ammonia lathered like soap and water, and are not decomposed by carbonic acid. The yellow matter even decomposes the alkaline carbonates in the cold, with effervescence, and likewise the solution of acetate of potassa, with the assistance of a gentle heat.

From these properties, it might be suspected, that this product was not pure, but rather in a state of intermixture; and accordingly, by the application of alkohol, it was found to consist of a small quantity of unctuous matter, which the alkohol takes up, and of an acid, which, from its colour, these chemists have named Yellow Acid. This acid, when freed from the fat which disguises its properties, is of a deeper colour, reddens more strongly the vegetable colours; it no longer melts, and does not exhale the odour of burnt grease, but fœtid and ammoniacal vapours. It combines with ammonia, which it deprives of its odour. Dissolved in fat, it communicates to it acidity and rancidness. Subjected to destructive distillation, it gives the usual products of the decomposition of animal matter.

The combination of the yellow acid with the fat, on being again submitted to the action of nitric acid, underwent no remarkable alteration, except that its colour changed from yellow to white, and its bulk and specific gravity were diminished.

The acid liquor obtained in the above process was next examined. It had a yellow colour: when saturated with carbonate of potassa, its colour changed to orange: afterwards it became turbid, and deposited a small quantity of orange-red powder. By distillation, a clear colourless liquor, of a rancid taste, containing a little ammonia, was obtained. On distilling the liquor, without the previous addition of carbonate of potassa, a similar colourless fluid passed over: what remained in the retort had become yellow by concentration: when concentrated, crystals formed in the midst of a liquor, viscid, and having an acrid bitter taste: on the addition of a little potassa, it became of a blood-red colour: mixed with alkohol, it gave a precipitate, consisting of a mixture of sulphate of lime and super-oxalate of potassa. It gave a second precipitate with lime water, consisting of oxalate of lime. After this double operation of alkohol and lime-water on this concentrated liquor, on being gradually evaporated farther, it became converted into a brown viscid syrup, of a bitter taste; which being again mixed with alkohol, threw down a copious precipitate of malate of lime, the alkohol retaining dissolved a portion of yellow acrid matter.

From these facts, it is concluded, to use the words of the memoir, "That the muscles contain potash, lime, and sulphuric acid, or perhaps sulphur burned by nitric acid: That a portion of the muscular fibre, or rather the cellular membrane with which it is enveloped, was converted by the action of the nitric acid into oxalic acid and malic acid. The alkohol employed in the separation of the malate of lime held in solution, 1st, A small portion of nitrate of lime; 2dly, A very bitter red-brown matter, possessing the flavour of walnut rhinds, of which more will be said hereafter; 3dly, A small quantity of that detonating matter already found in indigo: it was in this case obtained by concentrating the alkoholic solution, and separating it by the addition of carbonate of potash, in the form of granulated crystals, very inflammable, and very detonating."

"The disengagement of azotic gas, the formation of carbonic acid, of fat, of oxalic acid, and of a bitter substance, constitute the whole that was known respecting the treatment of animal substances by nitric acid: to this is now added the discovery, 1st, Of a yellow insipid matter, of little solubility, though acid, and which immediately succeeds the fleshy fibre; 2dly, Of another yellow matter, bitter, more soluble, and equally acid, which remains dissolved in the nitric liquor; 3dly, Of an inflammable detonating substance, which is also retained in solution; 4thly, and lastly, Of the formation of malic acid. It appears, and is the opinion of Messrs Fourcroy and Vauquelin, that the yellow and nearly insoluble matter is the first degree of change produced upon the muscular fibre: it passes quickly to the second degree of alteration and of acidity, whose product is the more soluble yellow matter:

this, by a third degree of alteration, is succeeded by the inflammable detonating substance, being the third and last term of the decomposing action of nitric acid. The authors of this memoir attribute the successive formation of these three compounds to the subtraction of part of the azote, and of a more considerable portion of the hydrogen; by this means the proportions of their elements are changed, and there remains an excess of carbon and of oxygen, which produces the state of fat and acidity already noticed. They examined if the acidity of the yellow substances might in any measure arise from nitric acid; but after a careful investigation, they were satisfied that it was in no degree present. The formation of oxalic and malic acids, belongs to the white mucous scales of the cellular membrane. Comparative experiments of the effects of nitric acid on the white membranaceous organs, which furnished plenty of these acids, and very little of the fat yellow matter, led the authors to this conclusion."

The yellow principle which they have thus discovered, appears to have some relation with the bile. According to the reporter of these experiments, the red matter of biliary concretions, when separated from the bitter green matter with which it is combined, displayed similar properties with the yellow fibrous matter. A substance similar to it too, was obtained from the urine of a person labouring under jaundice, by evaporating it, and treating it with alkohol. They suppose even, that it is it which gives the yellow colour to bile.

SECT. XI.

OF SKIN, CELLULAR FIBRE, AND MEMBRANE.

THE soft solids, enumerated under this section, have a close analogy in their properties, and appear to be the same matter under very slight modifications, or to have for their basis Gelatin.

The SKIN, which forms the external covering of the animal body, consists principally of two parts capable of being separated, and even possessed of different chemical characters; the external thin covering named the Cuticle or Epidermis; and beneath this, a thicker and more firm layer, the Cutis or true skin. Between these, has been also described by anatomists, a cellular texture, soft and gelatinous.

The first of these, the Cuticle, is nearly inorganic. When separated from the other parts, which it may be in the living animal, by the application of a blister, or when the skin has been detached, by maceration in hot water, it appears extremely thin and transparent. It is perfectly insoluble in water, even by long boiling, a property in which it differs from the true skin, which may be dissolved: it is merely softened, and at length reduced into small particles. It is equally insoluble in alkohol. Solutions of the alkalis, however, dissolve it easily, forming a kind of soap; a mutual action, which we perceive well exemplified between these substances, in rubbing a little of an alkaline ley between the fingers, the soapy feel being strong. Lime, too, acts on it as a solvent;

and hence the advantage of lime in the operation of tanning: it removes the epidermis, and allows the true skin to be penetrated with the tanning liquor from each surface. The acids decompose it: sulphuric acid forms with it a kind of soapy pulp, and at the same time chars it: nitric acid stains it yellow.

The true skin, or CUTIS, is much thicker than the epidermis, and consists of layers interlaced: it has considerable firmness and elasticity. When macerated in water, it swells and softens, and the blood and other animal fluids contained in it are dissolved. If it be boiled strongly in water, it is then entirely dissolved, and this solution presents all the characters of gelatin: it is precipitated by tannin, and by nitro-muriate of tin; and, when evaporated, forms a jelly or glue, more or less consistent. Seguin, in his researches on the art of tanning, had observed, that the skin in its dense state does not easily combine with tannin; he regarded it, therefore, as gelatin hardened by a slight degree of oxidizement; and on this hypothesis, he explained the effect of some substances, as the gallic acid, in promoting the operation of tanning; they partially de-oxidized it, he supposed, and thus facilitated its gradual combination with the tannin. Mr Hatchet, without assigning the cause, has observed also the difference between skin and pure gelatin, and likewise the differences in the skin of different animals, in the jelly or glue they afford by boiling with water. There is a gradation, he observes, from the most firm and consistent glue, a small portion of which communicates viscidity to water, to a tremulous mucilage. All of them are essentially gelatin, or possess its chemical properties; but they differ in the degree of consistence, which, when they are all in a solid state, they communicate to water, and in the facility with which they are acted on by tannin, nitro-muriate of tin, nitric acid, and other re-agents; those which are least consistent and viscid being dissolved, and acted on with most facility *. The most flexible skins, he found, always afforded gelatin more easily, and of a less viscid quality, than those which are less flexible; and in the arts, the different kinds of size and glue are prepared from the skins of different animals, according to the purpose to which they are to be applied, the skin being well cleaned, boiled in water until it is dissolved, and the decoction evaporated to the due consistence.

The art of tanning skin, from the operation of tannin on its gelatin, has already (p. 292) been described.

Acids act on skin, and decompose it. The nitric acid causes an evolution of nitrogen gas and prussic acid, and a formation of oxalic acid; the skin, or the glue formed from it, dissolves, and the liquor acquires a yellow colour, which becomes deeper when it is saturated with ammonia. Muriatic acid dissolves the glue formed from skin, and the solution suffers no change for many months.

Skin is also soluble in alkaline solutions. The glues formed from it, consisting of pure gelatin, are dissolved by them; and Mr Hatchet has remarked, that the compound is not soapy, as it is, when the gelatin is not pure but mixed with any membranous part not soluble in water.

Skin in its moist state is liable to putrefaction; less so, however, the more dense and firm it is; and this is ob-

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* Philosophical Transactions, 1800, p. 367, 368

served even in a state of solution, Mr Hatchet having remarked, that a solution of glue is much longer in showing signs of putrefaction than a solution of tremulous animal mucilage.

Skin is decomposed by heat, and affords the usual products of animal matter.

The CELLULAR FIBRE, or net-work, the Rete mucosum of anatomists, interposed between the cutis and cuticle, has been little examined, and indeed cannot be detached from the other parts. It is the seat of the colour; and this colouring matter can be acted on even through the cuticle, the skin of the negro being whitened by the action of oxymuriatic acid, as Dr Beddoes first ascertained, though the black colour is resumed in a short time.

The MEMBRANES, which compose so large a portion of the soft solids, forming the cellular texture, the coats of the vessels, and the coverings of the viscera, appear to be of the same nature. They have similar flexibility, and they dissolve more or less completely in water, forming gelatinous solutions.

SECT. XII.

TENDON. LIGAMENT. CARTILAGE. HORN. HAIR, &c.

THESE, in their physical properties, are different from the substances described in the preceding section, particularly in their greater firmness and hardness; and they form a gradation into those which are still more highly indurated, bone and shell. The chemical constitution of some of them has, however, been only imperfectly investigated. Ligament, tendon, and muscle, it is observed by Mr Hatchet, seem to glide almost imperceptibly into each other: they are connected with cartilage, as it is, on the other hand, with horn; and the basis of all them appears, from Mr Hatchet's experiments, to be albumen. I have therefore placed them under one section.

The TENDONS, which are cords or flat sheaths connecting the muscles with the bones, have a considerable degree of toughness and elasticity: their texture is fibrous. They are with difficulty acted on by water. It is said, however, that from long boiling they are dissolved, and their solution forms a jelly or glue. It is sufficiently probable, that they may afford so much gelatin as to form a gelatinous fluid; but it may be doubted if they are entirely soluble.

The LIGAMENTS connect and bind the bones together at their articulations: they are distinctly fibrous in their texture, the fibres running longitudinally; are possessed of great strength and cohesion; can be stretched out, and have a degree of elasticity, and are not easily broken. When boiled in water, they afford a portion of gelatin, the water being rendered turbid by infusion of tannin; but the entire substance cannot be dissolved, and it even often remains, after the boiling, with its texture little altered. It is obvious, therefore, that its basis is not gelatin, but appears rather to be indurated albumen.

CARTILAGE forms the transition to bone: it has so much induration, as to require the exertion of some force to bend it; and in a morbid state, it is often so highly indurated as to be ossified. Bone, on the other hand, is in the first stages of its formation and growth cartilaginous; it sometimes becomes so, too, from disease: and a cartilaginous matter exists in the hardest bones, and forms their basis, from which the other ingredients, the gelatin and earthy matter, may be removed by their proper solvents.

Cartilages are solid, but soft and easily cut; highly elastic, dense in their texture, white and semi-transparent. They cover the articulated extremities of bones, or sometimes form distinct parts.

The chemical properties of cartilage are not very well determined, and appear to vary in different cartilages. Thus Mr Hatchet has remarked, that "the cartilages of the articulations are completely soluble when long boiled with water; but this by no means happens when other cartilages are thus treated *." They are stated, however, to be softened by maceration in water, and by long boiling to be nearly entirely dissolved.

The little action exerted even by the more powerful chemical re-agents on cartilage, is very well shewn by the fact, that in subjecting a bone to the action of diluted muriatic or nitric acid, though the gelatin and the phosphate of lime are dissolved, the cartilaginous part remains undissolved, transparent, and presenting the figure of the bone. This residual cartilaginous matter, it is remarked by Mr Hatchet, "is not easily soluble in dilute acids; for (according to its texture) many weeks, and even

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* Hatchet, Philosophical Transactions, 1800, p. 370.

months may elapse, before a small part is taken up; but in concentrated nitric acid, or in boiling dilute acid, it is rapidly dissolved."

As the matter of cartilage thus obviously differs from gelatin, and as it is comparatively insoluble and inactive, it appears to be what Mr Hatchet has considered as indurated albumen, and which is the basis of a number of animal solids. He accordingly states this principle as the essential part of cartilage, horn, hair, feather, quill, hoof, nail, and shell, varying only in its consistency from a soft jelly to an elastic, brittle, and hard body like tortoise shell, but in all of these of similar chemical properties. From experiments on these bodies, which did not give any essential difference in the results, it appears, that this matter is softened when boiled in water, and the water becomes slightly turbid with nitro-muriate of tin, but suffers no change from the tanning principle. Muriatic and sulphuric acids had little effect on it unless heated; and the same was the case with nitric acid much diluted, or in the state proper to extract and separate gelatin; but if the immersion in the dilute acid was continued during some weeks, the acid gradually acquired a yellow tinge, and, when saturated with ammonia, became of a deeper colour without having its transparency disturbed. The substance macerated, is softened and becomes more transparent; if immediately immersed in pure ammonia, its colour changes to a deep orange, inclining to blood red, and it is gradually dissolved, forming a deep orange or yellowish brown liquor. If, when taken out of the acid, it is well washed in distilled water and then boiled, it is also dissolved and forms a liquor, precipitated like gelatin by infusion of tannin and nitro-muriate of tin. If the nitric acid was not sufficiently diluted, or if heat was applied, the whole was rapidly dissolved with effervescence, and a discharge of nitrous gas; and the solution presented nearly the same properties as that with the dilute acid. The fixed alkalis combine with this principle in all its varieties, and form saponaceous compounds, ammonia being disengaged during the combination, and charcoal precipitated. These compounds were decomposed by the addition of an acid, and a copious precipitate thrown down, soluble in an excess of acid, and capable, with the alkali, of again forming soap. This principle, when distilled, gave a small portion of water, some carbonate of ammonia, a fœtid empyreumatic oil, carburetted hydrogen, and carbonic acid gases and prussic acid. Its coal affords little saline matter, principally phosphates.

Mr Hatchet was induced to make some comparative experiments on pure coagulated albumen dried, and found them almost precisely the same. There can be therefore little doubt, that albumen is the basis of the substances above described, existing in them, with variable proportions of gelatin, and sometimes with phosphate and carbonate of lime.

These earthy salts do not appear to be essential to the constitution of cartilage, and when present are to be regarded, as Mr Hatchet has supposed, as extraneous or foreign to the composition *.

The chemical nature of **Horn**, is very similar to that of cartilage; and, with regard to physical qualities, it differs from it in little except in its greater degree of induration. It is hard, so as not to be easily bent, unless when artificially softened, but it can be easily pared or cut; its texture is close and smooth, and it is more or less transparent, according to its thickness. When heated, horn is softened, and it is then capable of being moulded into any form.

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* Philosophical Transactions, 1799.

Shavings and pieces of the horns of different animals, when boiled a long time in water, were found by Mr Hatchet to afford small quantities of gelatin; discovered by being precipitated by the tanning principle, and by nitro-muriate of tin: the most flexible horns yielded the largest quantity of gelatin, and most easily; and when deprived of it, and allowed to dry spontaneously, they became more rigid and more easily broken: this residual matter Mr Hatchet regards as indurated albumen. He found farther, that they yield a very small quantity of phosphate of lime, so that it can scarcely be regarded as an essential ingredient. Thus, 500 grains of the horn of the ox, afforded, after a long continued heat, only 1.50 grains of residuum, and of this, less than half proved to be phosphate of lime *.

These observations apply to the horns of the ox, ram, goat, and chamois: it is singular, that the stag's or buck's horn is of a very different nature, as is evident from the products it has been long known to afford, when decomposed by heat, which are perfectly analogous to those of bone. Mr Hatchet has accordingly remarked, that like

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* Philosophical Transactions, 1799, 1800.

bone it affords much phosphate of lime, and a large quantity of gelatin.

HOOF appears to be not only of a mechanical structure, but likewise of a chemical composition similar to horn; the shavings of ox's hoof, when long digested in water, affording, as Mr Hatchet found, a liquor which was only made slightly turbid by nitro-muriate of tin.

The matter of the **NAIL** is in like manner softened only, by digesting in boiling water for several days, and affords a slight cloud on the addition of nitro-muriate of tin.

Similar results, too, were afforded, in Mr Hatchet's experiments, by the horny scales of serpents and lizards, as well as of certain insects, and by tortoise shell; and there can be little doubt that these are of the same chemical composition as horn.

FEATHER and **QUILL**, chemically considered, appear to be similar to these, and to have the same basis of indurated albumen. Digested in boiling distilled water for ten or twelve days, they did not afford any trace of gelatin by the test of the tanning principle, but nitro-muriate of tin produced a faint white cloud.

Even **HAIR**, though apparently very remote from some of these substances in mechanical structure, appears, at least with regard to its basis, to be the same, or nearly so, in chemical composition. Mr Hatchet found, that when it was long digested or boiled with distilled water, it, like them, imparted to the water a small portion of gelatin, which was precipitated by tannin, and by nitro-muriate of tin; and when the hair had been thus deprived of gelatin, and was subsequently dried in the air, the original flexibility and elasticity of it was much diminished; it was also little liable to farther spontaneous change, and had all the characters of the matter which Mr Hatchet regards as indurated albumen. Vauquelin has more lately submitted it to a more minute examination. He found, that though insoluble in water boiling under a common pressure, it may be dissolved in Papin's digester, where the temperature is higher from the pressure being increased,—a fact indeed before observed by Achard. If the temperature was raised high in this instrument, the hair even suffered decomposition, carbonate of ammonia, empyreumatic oil, and sulphuretted hydrogen being evolved. When the solution of hair is thus effected at a high temperature, an oily matter is always evolved; the solution freed of this, gives copious precipitates with infusion of galls and with oxymuriatic acid. It is also rendered turbid by the other acids, but an excess of acidity restores its transparency. It does not gelatinize, even when much concentrated by evaporation. A dilute solution of potassa, he found, dissolves it, hydro-sulphuret of ammonia being at the same time evolved, while a little oil, sulphur, and iron, remain undissolved: this alkaline compound, according to Chaptal, is a soap. The acids too, gradually dissolve and decompose it, nearly with the same results as are given by analogous animal substances. Alkohol digested on hair, extracts a portion of oil, or rather two oily fluids differing in their colours, and differing too according to the colour of the hair itself. From black hair, there first separates, as the alkohol cools, an oily matter in white scales; and afterwards, on evaporating the oil, a concrete dark coloured oil: from red hair there are obtained, in a similar manner, first a white, and afterwards a red oil: the colour of the hair seems to reside in this oily matter, and also, as Vauquelin supposes, in the darker coloured hair, on sulphuretted iron. He found hair, on incineration, to afford phosphate, sulphate, and carbonate of lime, muriate of soda, silex, and oxides of iron and manganese, the whole amounting to a very small proportion of the hair, and varying in hair of different colours.

The structure of hair appears perfectly close, and its external surface, even when viewed with the microscope, smooth. Yet, as Monge has observed, it is certain that the surface is not equally smooth when rubbed in different longitudinal directions, but is composed either of scales like those of fish, or imbricated zones like the horns of animals; hence its tendency to be entangled: and on the same property is founded the art of felting hair, subservient to that of hat making. The details of this art are very well stated and explained by Chaussier *, and in a memoir by Mr Nicholson †, to which some facts have been added by an anonymous correspondent ‡.

WOOL is to be regarded merely as a finer kind of hair. It has not been examined with much minuteness, but it possesses one characteristic property of what Mr Hatchet regards as indurated albumen, and as the basis of all those substances, that of forming a soap with alkalis. It has this even in so high a degree, that some years ago it was proposed by Chaptal, to be employed as a substitute for oil or fat in the manufacture of soap; woollen rags or

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* Nicholson's Journal, 4to, vol. i. p. 399.

† Ibid. vol. iii. p. 23. ‡ Ibid. p. 73.

clippings of wool being boiled in an alkaline ley to saturation: the product is a soft soap of a grey colour, soluble in water, and possessed of sufficient detersive power*. It has not been established in use, partly as it gives a grey colour to the thread or cloth which is difficult to remove, and hence could not be applied to linen, and partly from its very disagreeable smell, which is only imperfectly removed by long exposure to the air. It is not improbable, however, that it may be used with advantage in cleansing wool previous to dyeing; and from the observations of Chaptal, it is probable even that it may act as a mordant.

From the experiments of Berthollet it appears, that wool acted on by nitric acid affords oxalic acid and a fatty matter; the same products, with a less proportion of the former, being afforded by hair. He found too, that wool is dissolved both by sulphuric and muriatic acids, ammonia being formed, and charcoal deposited.

With the substances, the chemical history of which has now been given, may lastly be associated SILK, as strictly connected with them in properties and chemical relations. The fibres of silk are spun by the caterpillar of a species of phalena, the Phalena bombyx, a native of China: the silk worms, however, have been naturalized in a number of countries. The silk is inclosed in two small bags, in very fine fibres of different shades of colour, from a white to a more or less faint yellow or red, shining from a varnish with which it is naturally covered, and from which it likewise derives stiffness and elasticity: this varnish is soluble in water, but not in alkohol; and its watery solution gives a precipitate with tannin, and with several metallic salts. The colouring matter appears also not to be essential to silk; it is soluble in alkohol, and approaches in its properties to a resin. To adapt it to use, silk is freed from these foreign substances, principally by the action of weak alkaline leys, soap, alkohol, and diluted acids, and especially the muriatic acid diluted with alkohol according to the process for bleaching silk, discovered by Beaumé *.

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* Nicholson's Journal, 4to, vol. i. p. 40.

Silk is not soluble in water, even at a boiling heat: it is equally insoluble in alkohol. The alkaline leys dissolve and at the same time decompose it, ammonia being evolved. The acids erode and dissolve it. Nitric acid renders it yellow, disengages nitrogen gas, forms prussic acid, and, according to Berthollet, oxalic acid, with a portion of fatty matter. This action was more particularly examined by Welter †; and he discovered, that, by the repeated distillation of nitric acid from silk, a peculiar matter, which he named Bitter Principle, was formed: it is of a golden yellow colour, soluble in water and in alkohol, capable of crystallizing on cooling, inflammable, and having a very bitter taste, and which appears to be the same substance as the yellow bitter acid more lately described by Vauquelin, and already noticed, as formed by the action of nitric acid on the muscular fibre.

Silk is decomposed by heat, and affords the usual products of animal matter. The proportion of carbonate of ammonia is very large.

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* Nicholson's Journal, 4to, vol. i. p. 32.

† Annales de Chimie, tom. xxix. p. 301.

The silk-worm forms an acid liquor, which was imperfectly examined by Chaussier. On the supposition that it was a particular acid, it received in the new nomenclature the name of Bombic Acid; but there is much reason to suppose, that it and some other acids formed by insects, as that by the ant, which has been named Formic Acid, are acetic acid slightly disguised.

SECT. XIII.

BONE AND SHELL.

THE substances to be described under this section are distinguished by the large quantity of earthy matter which enters into their composition, and communicates to them solidity, hardness, and other characters; phosphate of lime being predominant in bone, carbonate of lime in shell, though each frequently contains portions of both these earthy salts, and sometimes phosphate of magnesia.

BONE, which composes the most solid and hard part of the animal frame, giving figure to the whole, and serving as the support of motion, and the covering with which many of the organs are protected, presents some varieties of structure, and still greater diversities of form In general, the bones appear to be composed of laminæ in more or less perfect adhesion. Flat bones are dense towards the surface, while, in the middle or inner part, the laminæ separate, and the texture is spongy. In the long cylindrical bones, the external surface is likewise dense; but towards the inner part the density is diminished, a spongy or cavernous structure is apparent, and there is a cavity, in which a matter of a fatty nature, the marrow, is contained; and a portion of this appears even to be diffused through the more dense part of the bone. Externally, the bones are covered by a membrane, the Periosteum, and they are penetrated by blood-vessels, absorbents, and nerves.

Bone admits of a very simple analysis, by which its immediate principles are discovered. When boiled in water, the decoction is found to contain a considerable portion of gelatin, and, if the boiling has been long continued, even concretes into a jelly on cooling. If the bones be previously rasped, the quantity of gelatin obtained is much larger; and in this way, as Proust has shewn, bones may be economically used to prepare a nutritious article of diet [*].

If a piece of bone be digested in dilute muriatic or nitric acid, the gelatin and the earthy matter are dissolved, and there remains at length a firm cartilaginous substance, presenting the figure of the bone. By this experiment, then, cartilage is proved to be a constituent of bone.

If bones be calcined in an open fire, the animal matter they contain is decomposed and burnt out; they soon lose their charred appearance, and are at length converted into a white earthy-like substance, still retaining the figure and even the structure of the bone. This is what the chemists formerly considered as the earth of bones, and of the nature of which they were ignorant. Gahn and Scheele discovered it to be phosphate of lime. It is likewise separated during the decoction of bone in water, especially when the boiling has been performed under an increased pressure, by which the temperature is more elevated, the cartilage softened, and the gelatin completely dissolved; and can also be dissolved by the action of an acid on bone.

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[*] Nicholson's Journal, 8vo, vol. i. p. 100.

During the boiling of bones in water, a portion of fatty matter separates, and collects on the surface. It is uncertain, however, how far it may be derived from the marrow mechanically diffused through the bone, and can perhaps scarcely be considered as essential to the bony matter.

By these experiments, then, bone is proved to consist, independent of this unctuous matter, of gelatin, cartilage, and phosphate of lime. Some other principles appear even to be contained in smaller quantity. Carbonate and sulphate of lime are found in burnt bones; a little carbonate exists in the recent bone; but the greater part of it found in the burnt bone, as well as the sulphate, appear to be products of the combustion, while the phosphate of lime is evidently an essential ingredient. In the bones of the inferior animals phosphate of magnesia has been discovered by Fourcroy and Vauquelin, while they could discover no trace of it in human bones; a singularity which, they observe, is probably connected with the fact, that phosphate of magnesia is contained in the urine of man, but not in that of other animals; that, therefore, this earth is discharged from the human system by this excretion, instead of being deposited in the bones.

The proportions of these principles must differ in bones in different states: in the bones of young animals, the gelatin and cartilage are in larger proportion than in more advanced age. The quantity of gelatin extracted by boiling in water is from 25 to 50 from 100 parts, and the remainder is principally phosphate of lime. The phosphate of magnesia is always in very small quantity, not exceeding two in 100 parts. Ox-bone, according to an analysis, given by Fourcroy and Vauquelin, consists of gelatin 51, phosphate of lime 37.7, carbonate of lime 10, phosphate of magnesia 1.3 *. Fish bones, according to Mr Hatchet, contain more cartilaginous matter relative to the phosphate of lime than the bones of quadrupeds.

The following table has been given by Merat-Guillot, of the composition of the bones of different animals, and some similar substances, the proportions being referred to 100 parts †.

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* Nicholson's Journal, vol. viii. p. 87.

† Annales de Chimie, tom. xxxiv. p. 71.

	Proportion of Gelatin.	Proportion of Phosphate of Lime.	Proportion of Carbonate of Lime.	Loss.
Human bones from a burying-ground.	16	67	1.5	15.5
Dry human bones, which had not remained in the earth	23	63	2	2
Bone of the ox	3	93	2	2
—— of the calf	25	54		21
—— of the horse	9	67.5	1.25	22.25
Teeth of the horse	12	85.5	0,25	2.25
—— of the elephant, or ivory	24	64	0.1	11.15
Bone of the sheep	16	70	0.5	13.5
—— of the elk	1.5	90	1	7.5
—— of the hart	27	57.5	1	14.5
—— of the hog	17	52	1	30
—— of the hare	3	85	1	5
—— of the chicken	6	72	1.5	20.5
Egg shells	3	2	72	23
Bone of the pike	12	64	1	23
—— of the carp	6	45	0.5	48.5
—— of the viper	21.5	60.5	0.5	17.5
—— of the lobster	18	14	40	28
Mother of pearl	2.5	0	66	31.5
Crab stones	2	12	60	26
White coral	1.5	0	50	48.5
Red coral	0.5	0	53.5	46
Articulated coral	7.5	0	49	43.5
Cuttle fish scale	8	0	68	24

From the composition of bones may be better understood the changes they suffer from heat, or from the operation of re-agents.

When exposed to heat in close vessels, a very large quantity of carbonate of ammonia, with a portion of fœtid oil, are obtained from the decomposition of the gelatin; and this process is even followed on a large scale, to procure the ammonia. The water which distils over, contains also, according to Fourcroy, a little prussic and sebacic acids saturated with ammonia, and carbonic acid: carburetted and sulphuretted hydrogen gases are disengaged during the distillation. When heated in an open fire, the oil they contain is melted, appears on their surface, and is converted into vapour, which burns with a fœtid odour; the products of the decomposition of the gelatin and cartilage being at the same time disengaged. The bone retains still its figure; is charred; but by continuing the application of heat, with a free current of air, it may be burnt perfectly white, or there remains merely the earthy salts of the bone. This forms a porous mass, which cannot be vitrified but by a very intense heat.

The analysis of burnt bones is effected by the agency of the acids. When the acid is added to the burnt bone in powder, a lively effervescence is excited, from the disengagement of the carbonic acid of the carbonate of lime; the gas has, at the same time, a pungent smell, which has been ascribed to the presence of prussic acid. If sulphuric acid has been employed in the decomposition, a large quantity of sulphate of lime is formed, and a super-phosphate of lime is produced, soluble in water, and therefore carried off by washing,—a process which, as has been already remarked, is followed to procure that acid for the preparation of phosphorus. If, instead of sulphuric, nitric acid be employed in the analysis, the constituent parts of the burnt bone are better discovered. It is entirely dissolved; the carbonic acid of the carbonate of lime contained in the burnt bone is disengaged during the solution, and may be collected: the phosphate of lime, according to the mode of analysis first employed by Scheele, may be at least partially decomposed by sulphuric acid, sulphate of lime being precipitated, and phosphoric acid remaining with the nitric acid and part of the lime. According to a more exact method, the phosphate of lime may be precipitated by the addition of pure ammonia: by adding to the residual liquor nitrate of barytes, sulphuric acid is detected; and from the quantity of precipitate, the proportion of sulphate of lime, from the decomposition of which it had originated, may be inferred: and to discover the quantity of lime which had been combined with the carbonic acid disengaged during the solution, Mr Hatchet added carbonate of ammonia, and obtained a precipitate of carbonate of lime,—a method not altogether unexceptionable, since the precipitate might in part at least arise in consequence of the operation of a complex affinity from the sulphate of lime in solution; or, where this had been decomposed by a previous addition of nitrate of barytes, from the nitrate of lime which must thus have remained in the liquor. The quantity produced, however, Mr Hatchet observes, was much greater than the quantity of sulphuric acid, indicated by the precipitation by barytes, could have saturated; and hence, as well as from the disengagement of carbonic acid during the solution the existence of carbonate of lime in the burnt bone is demonstrated. The phosphate of magnesia, which Fourcroy and Vauquelin discovered in the burnt bones of the inferior animals, was detected by precipitating the liquor obtained by washing the mixture of burnt bones and sulphuric acid, which had stood for some days, by ammonia, adding the ammonia in excess. The precipitate consists of phosphate of lime and phosphate of magnesia and ammonia: to separate these, it was boiled in a solution of potassa, which disengages the ammonia, and attracts the acid of the magnesian-ammoniacal phosphate, leaving the magnesia mixed with the phosphate of lime. These are separated by boiling them in acetous acid, which dissolves the former, leaving the latter undissolved: from the solution of acetate of magnesia, the magnesia may be precipitated by carbonate of soda; and the carbonate of magnesia, if free from lime, will form a transparent solution with sulphuric acid *.

The sulphate and carbonate of lime, indicated by the analysis in calcined bone, or at least the greater part of them, may, as has been already remarked, be products of the calcination, and not constituent parts of the bone. In the bony matter, there probably exists more lime than the phosphoric acid can saturate; carbonic and sulphuric acids will be formed during the calcination of the bone, from the decomposition of the animal matter, of which the bases of these acids are elements; and the acids thus formed will be attracted by the excess of lime. A portion of carbonate of lime is indeed indicated in recent

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* Nicholson's Journal, vol. viii. p. 86.

bone by Mr Hatchet's experiments, a slight effervescence attending its solution in an acid; but the quantity appears to be inconsiderable, and by Merat-Guillot it is stated, in the bones of land animals, to amount to not more than 1.5 in 100 parts*.

The entire quantity of lime and of phosphoric acid contained in bones, may probably be best determined by the method pointed out by Fourcroy and Vauquelin,—precipitation of the lime by oxalic acid from the solution of the calcined bone in diluted nitric acid. The liquid may be evaporated, and by a strong heat the nitric acid expelled, leaving the concrete phosphoric acid; or the phosphoric acid may be precipitated by acetate of lead.

The acids, as has already been remarked, act on recent bone, dissolve its earthy matter and its gelatin, leaving the cartilaginous part undissolved; and from this solution phosphate of lime may be precipitated by an alkali,—a proof of its previous existence in the bone.

The alkalis have scarcely any effect on the earthy matter of bones, but they dissolve their gelatinous and oily matter.

The earthy substance of bones, it has been already remarked, has a strong attraction to some varieties of colouring matter; and hence the bones of a living animal can be tinged by such colouring substances mixed with their food.

Bones are not much liable to spontaneous decomposition; even the animal matter they contain suffers little change for a very long period; the re-action of its elements, as well as the action of air and humidity, being in a great measure prevented by the solidity communicated by the phosphate of lime.

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* Annales de Chimie, tom. xxxiv. p. 71.

Fossil bones, or those which have been long buried in the earth, and have in consequence undergone some changes, particularly from the infiltration of carbonate of lime, were examined by Mr Hatchet. The animal matter appeared to have been completely removed; and the phosphate of lime remained intermixed with the carbonate of lime which had been introduced; the latter substance, by its chemical agency, probably having contributed to the decomposition of the animal matter.

The body of the teeth of animals is evidently bone; and accordingly, it has been found to present the same chemical results. It dissolves, Mr Hatchet remarks, with a feeble effervescence in dilute nitric acid, leaving its cartilaginous basis retaining even the shape of the tooth. But the external covering, or ENAMEL, is somewhat different. Mr Hunter remarked, that when immersed in an acid, it left no cartilaginous part,—an observation confirmed by Mr Hatchet, who likewise found, that when exposed to heat, it emitted little or no smoke or empyreumatic odour. Josse, in his examination of the teeth, obtained the same results, and, when boiled in water, the decoction gave so slight a precipitate with tannin, as scarcely to indicate the presence of gelatin; neither was it at all softened by boiling in water under increased pressure *. It appears, therefore, to be nearly destitute of animal matter. It dissolves readily in acids, with a slight effervescence, as Dr

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* Nicholson's Journal, 8vo, vol. x, p. 38.

Blake remarked, and Josse has confirmed, and appears therefore to consist of phosphate, with an intermixture of carbonate of lime.

The presence of fluoric acid combined with lime in the enamel of teeth was announced by Morichini, an Italian chemist. He first observed it in the enamel or outer layer of the fossil teeth of the elephant, which he found to be composed almost entirely of fluate of lime, while the body of the teeth was composed of phosphate. And on afterwards submitting the enamel of human teeth to the same trials, he found, that it too contained a large proportion of fluate, vapours of fluoric acid being exhaled when the enamel was acted on by sulphuric acid. Gay Lussac so far confirmed this discovery, as to prove the existence of fluate of lime in ivory, copious vapours of fluoric acid being exhaled from it when concentrated sulphuric acid was poured upon it *. And with this the more recent experiments of Fourcroy and Vauquelin agree †. These chemists have been unable, however, to discover the fluoric acid in the enamel; and Mr Brande likewise found, that when this substance is subjected to the action of sulphuric acid aided by heat, no vapours but those of sulphurous or sulphuric acid are exhaled ‡.

The SHELLS with which the bodies of many marine, and also a number of land animals are covered, are obviously analogous in their structure to bone.

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* Philosophical Magazine, vol. xxiii. p. 264.

† Ibid. vol. xxv. p. 265.

‡ Nicholson's Journal, vol. xiii. p. 214.

therefore interesting to determine, how far shell is similar to bone in its chemical composition. The general difference between them was known; for, while phosphate of lime is the basis of the one, it was known, that carbonate of lime exists in much larger quantity in the other. Mr Hatchet undertook the examination of this subject, and, as the result of it, established, that shell and bone, in their different varieties, constitute as it were two genera, in both of which animal matter is contained, but in the one this is indurated by phosphate, in the other by carbonate of lime; and these are connected by a certain order of substances,—the crustaceous coverings of certain marine animals, and likewise some of the species of zoophytes, in which, with the animal matter, are intermixed variable proportions both of carbonate and phosphate of lime.

In Mr Hatchet's experiments, the shell submitted to examination was immersed in acetous acid, or nitric acid diluted with four, five, or six parts of water. The carbonate of lime was precipitated by the carbonate of ammonia or potassa; and phosphate of lime (if present) was previously precipitated by pure ammonia. If any other phosphate, as that of soda, was suspected, it was discovered by acetate of lead.

The greater number of marine shells, he observes, are of two descriptions, either of a porcellaneous aspect, with an enamelled surface and fibrous texture, or they are composed of the substance called Nacre or Mother of Pearl. The first kind dissolved in the acids with strong effervescence, and their solutions afforded no trace whatever of phosphate of lime, or of any other combination of phosphoric acid. They contained only carbonate of lime;

and the animal matter which acts as a cement to this, and which Mr Hatchet considers as albumen in various states of induration, is in small proportion; hence, when the shells are exposed to heat, they exhale little empyreumatic animal odour; they emit no smoke: and when dissolved in acids, little or no vestige of it can be discovered by any flocculent or gelatinous residuum.

In shells of the other description approaching to nacre, the earthy matter is also carbonate of lime, but is present in much smaller proportion, while the animal matter is in large quantity. Hence these shells give much smoke, and a strong empyreumatic odour, when exposed to heat, and when acted on by acids, give out less carbonic acid, and leave a large quantity of a membranaceous or cartilaginous residuum, retaining often the figure of the shell. This substance often constitutes a large part of the shell, as in that of the oyster or muscle, and is so much indurated as to be no longer gelatinous; and in all the shells of this division, it appears to be deposited in layers, each having a corresponding coat of carbonate of lime. Mother of pearl itself, and likewise pearls, were found to be of similar structure and composition. Their waved appearance and their iridescence, are evidently the effects of this lamellated arrangement, and of the nebulous semi-transparency of the substances composing it.

An extensive class of substances,—the zoophytes, comprehending the varieties of madrepore, millepore, tubipore, were found to consist likewise of carbonate of lime with animal membrane.

Mr Hatchet found, that the substance analogous to shell, which covers crustaceous marine animals, echini, crab, lobster, &c. is of different composition. It had indeed the same cementing animal matter, but with this were united both carbonate and phosphate of lime, forming therefore a substance intermediate between bone and shell. The shells of the eggs of birds were of similar composition; and even some of the zoophytes, as various species of isis, gorgonia, &c. gave indications of phosphate of lime being intermixed with the carbonate of which they were principally composed.

SECT. XIV.

FAT. SPERMACETI. SEBACIC ACID.

FAT appears to be a peculiar secreted matter, as no traces of it can be discovered in the blood. As it exists in the animal body, it is nearly fluid, and is retained in distinct minute cells: after death it is found more or less solid, and its solidity varies in different animals. To procure it free from the animal fluids and cellular fibre mixed with it, and sufficiently pure for chemical or pharmaceutical purposes, it is cut and washed in water, is then melted with a very gentle heat, a little water being added, to prevent it from being scorched. Fat prepared in this manner, is named Axunge or Lard when soft, when of a firmer consistence it forms Tallow, and from some animals, as from the whale, and other marine animals, it is obtained perfectly fluid, forming animal oil.

Animal fat has properties nearly the same as those of vegetable expressed oil. It is insipid and inodorous, insoluble in water and in alkohol, and is capable of being combined with the alkalis, so as to form soap. It is inflammable, and cannot be volatilized unchanged.

Fat, when exposed to a warm atmosphere, is liable to become rancid, more so than the vegetable oils. This rancidity appears to be owing to an absorption of oxygen, and a consequent formation of an acid, either from the oxygenizement of the fat itself, or of the gelatinous matter mixed with it. This acid may be abstracted by washing with water or alkohol, when the sweetness of the fat is in some measure restored, while the water acquires the power of reddening the vegetable colours.

Fat melts from a very moderate heat; lard becomes fluid at 92°, tallow and the firmer fats require a heat somewhat higher. By continuing the heat or raising it above the melting point, it suffers decomposition, pungent vapours arise from it; and when it is allowed to cool, it is found acrid and of a yellow colour.

A similar decomposition is effected, by distilling fat in close vessels: an acid liquor passes over, with an empyreumatic oily matter, partly liquid and partly in a concrete state; a quantity of elastic fluid, consisting of carburetted hydrogen and carbonic acid, is disengaged, and the residuum is mixed with charcoal: and by repeating the distillation of the oily matter, a new formation of these products takes place, until the whole is decomposed. The acid produced in this distillation, named the Sebacic, has been considered as a peculiar one, the properties of which are to be immediately stated.

From the products of this decomposition, fat, like expressed oil, appears to be a compound of carbon, hydrogen, and oxygen. Ammonia is also mingled with the products in small quantity, derived from nitrogen either existing in the composition of the fat, or derived from the animal matter mixed with it.

Fat is highly inflammable, and in burning gives much light; hence its common use for this purpose; it is probable, that by the high temperature in the wick according to the common method of burning it, it is decomposed and converted principally into a gas of the nature of olefiant gas, as has been already explained under the history of vegetable expressed oil, from the combustion of which the light originates. The products of this combustion, are water and carbonic acid.

Fat is acted on by the acids, and the result is different according to the acid to the action of which the fat is subjected, and the manner in which it is applied. If nitric acid be added in small quantity, it is supposed to be entirely decomposed, its oxygen abstracted by the fat, and what has been named by the French chemists Oxygenated Fat formed. The process they have given, and which has been received into the Pharmacopœia, is to add to melted lard one-sixteenth of nitric acid, stirring them thoroughly, and keeping the mixture fluid for some time. Nitric oxide and nitrogen gases are evolved, and the lard becomes granular and of a firmer consistence. If washed with water, any remaining nitric acid is removed. By distilling nitric acid repeatedly from fat, Gren obtained acetic and oxalic acids. Sulphuric acid, even in very small quantity, chars fat, rendering it brown or black. Muriatic acid exerts no action upon it.

Fat combines with the alkalis, forming saponaceous compounds.

Fat, like the expressed oils, is capable of combining with sulphur and with phosphorus, when their mutual action is aided by a moderate heat. It unites too with a number of the metallic oxides, and forms with them compounds more firm than the fat itself. From its facility of oxidizement it can even be made to act on the metals. Thus, if copper be covered with grease, and left exposed to the air, its surface soon becomes quite green; and quicksilver triturated with lard, forms an ointment of a blue colour, which becomes deeper on keeping, and from which at length scarcely any of the quicksilver can be obtained in its metallic form. In such cases sebacic acid is probably formed by the oxygenizement of the fat, and acts on the metal.

THE acid which is formed from the decomposition of fat by heat, it was observed by Bergman, resembled, in the saline combinations it formed, the acetic; and Gren considered it as precisely the same with that acid. Still, however, it presented some differences; it continued to be regarded as a peculiar acid; and in the modern nomenclature was named the Sebacic. Various processes were given for preparing it, of which one long ago proposed by Guyton affords it most easily, and has been generally followed. Fat is melted in an iron pot over a naked fire, quicklime in powder is added to it, stirring it continually, and increasing the heat. When the mixture has cooled, on boiling it in water, a brown acrid salt is obtained by evaporation of the solution, which was considered as the sebate of lime; by exposing it to heat in a crucible the remaining oily matter, to which the colour is owing, is decomposed, and the salt is obtained pure and white, by solution and crystallization. If sulphuric acid be poured on it, the sebacic acid is disengaged, and being volatile, may be obtained by distillation. The acid is formed in this process, by the decomposition of the fat by the high temperature, and is prevented from being dissipated by its combination with the lime. As obtained by distillation, it is a liquid having an acrid suffocating odour, exhaling a white vapour when in a concentrated state, and in this state having somewhat of an oily appearance. It reddens the vegetable colours, is very volatile, and, when transmitted through an ignited tube, is resolved into water, carbonic acid, carburetted hydrogen, and charcoal. Its salts are in general soluble and crystallizable.

This acid has, however, been more lately examined by Thenard *; and, according to the result of his researches, it is merely the acetic acid, the pungency of its odour being probably derived from a little sulphurous acid. According to this chemist, there is, however, a real sebacic acid, which had not been before observed, and which is possessed of very different properties. It is obtained by distilling lard, and treating the product with hot water: to the liquor thus procured acetate of lead is added: a flaky precipitate is formed, which is collected, dried, and heated in a retort with sulphuric acid. The liquid condensed in the receiver in this operation had no acidity; but there floated on the matter in the retort a substance

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* Nicholson's Journal, 8vo, vol. i. p. 34.

like fat, which was separated, washed, and boiled with water. The water entirely dissolved it; and, by refrigeration, crystalline needles were deposited, acid, and possessed of peculiar properties. They were also procured, merely by treating distilled fat with water, filtrating and evaporating the liquor.

This acid, which Thenard regards as the Sebacic, is, according to the enumeration which he has given of its properties, without smell: its taste is slightly acid: it melts like a kind of fat, reddens tincture of turnsole, and is much more soluble at a high than at a low temperature: boiling water saturated with it even becomes concrete by refrigeration: alkohol dissolves a large quantity of it: it crystallizes in small needles, or, by proper precautions, may be obtained in the form of large lamellæ of a brilliant appearance. It precipitates acetate and nitrate of mercury and of lead, and nitrate of silver: it neutralizes the alkalis, and forms with them soluble salts: that with potassa does not attract moisture from the atmosphere: it has little taste, and is decomposed by sulphuric, nitric, or muriatic acid. It does not render turbid the solutions of lime, barytes, and strontites. These properties are peculiar, and are considered by Thenard as sufficient to distinguish this acid from every other. Acetic acid is always formed along with it, and may be obtained by saturating the product of the distilled fat with potassa, and decomposing it by sulphuric acid, applying heat to volatilize the acetic. The strong and pungent smell of distilled fat, he observes, does not depend on any acid, since the colour of litmus is not changed when exposed to the vapour; but depends probably on a portion of the fat volatilized, and partially changed.

Spermaceti differs in some of its qualities from fat. It is found in the head of a species of whale, the Physeter macrocephalus, in an unctuous mass, from which a quantity of oil is obtained by expression. There remains a flaky substance, which is purified by melting, washing with water, and with a weak alkaline solution. This is spermaceti. It also exists in the oils of other species of whale, and is often spontaneously deposited.

Spermaceti is in masses of a flaky crystalline texture, soft, but brittle, white and brilliant, but sometimes having a yellow tinge from long exposure to the air. It is less fusible than fat; its melting point, according to Bostock and Irvine, being 113°. By raising the heat sufficiently, it may be volatilized, and passes over by distillation with little alteration. By subjecting it to this, however, repeatedly, it is decomposed, a quantity of acid is formed, and a liquid oil formed. Spermaceti is inflammable, and burns with a clear white flame.

A property in which it eminently differs from fat and expressed oil, is its solubility in alkohol and in ether. In alkohol it is dissolved sparingly; 150 times its weight of boiling alkohol being requisite, according to Dr Bostock's experiments, to dissolve it, and the whole precipitating as the fluid cools. Warm ether dissolves it rapidly; and by cooling it is precipitated so abundantly, as in appearance to convert the whole into a solid crystallized mass *. It is also dissolved with facility by oil of turpentine gently heated, and is deposited as it cools.

The alkalis act on spermaceti, and form saponaceous

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* Nicholson's Journal, vol. iv. p. 134.

compounds; less perfect however, and less soluble in water, than the soap from fat. A solution of pure potassa dissolves it, and the compound is soluble in warm water. Ammonia does not act on it when cold, but when boiling unites with it readily, and forms an emulsion, not decomposed by cooling or by the addition of water, but instantly decomposed by an acid [*].

The acids have little effect on it: concentrated sulphuric acid dissolves it, and changes its colour; and water precipitates it from this solution.

In its properties this substance evidently bears a strong resemblance to the matter which principally composes biliary calculi, and to that which is formed by the slow decomposition of muscular fibre,—a matter which Fourcroy has distinguished by the name of Adipocire, as being intermediate between fat and wax.

SECT. XVII.

CEREBRAL PULP.

THE soft matter which constitutes the substance of the brain and nerves, is evidently different, in its physical qualities, from any other animal substance. It has been examined by Fourcroy, with the view of determining its chemical characters.

In its consistence it is soft and pulpy: it soon suffers spontaneous decomposition when exposed to the air, but, when immersed under water, remains long without suffering much change. Dried by the heat of a water-bath, it first coagulates, and a small quantity of water separates from it. When dried and urged with a strong fire, it exhales ammonia, swells, becomes black, melts and diffuses acrid fumes : it then inflames if the air is admitted, and sulphurous acid is formed from its combustion. When decomposed in close vessels, the products are oil, carbonate of ammonia, carburetted and sulphuretted hydrogen, and carbonic acid gases, with some traces of phosphates of lime and soda in the residual charcoal.

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[*] Bostock, Nicholson's Journal, vol. iv. p. 134.

When the cerebral pulp is diluted with water, it is coagulated by heat, flocculi separating ; the liquor separated from these gives a precipitate with lime-water, and affords phosphate of soda by crystallization. Alkohol likewise produces coagulation ; as do the acids ; indicating, therefore, a principle analogous to albumen. Sulphuric acid, in coagulating, at the same time re-acts upon it, an oily matter being evolved. Nitric acid diluted disengages nitrogen gas, with considerable effervescence ; and phosphate and oxalate of lime, and oxalate of soda, are found in the residual liquor. Muriatic acid equally produces coagulation ; and the ley affords salts, the bases of which are soda and lime, neutralized partly by the muriatic, and partly by phosphoric acids.

The alkalis dissolve this matter. Potassa acts upon it in the cold, causing an evolution of ammonia : when heat is applied, the compound is saponaceous.

By the action of alkohol, not only is the matter analogous to albumen separated, but another substance is obtained similar to some of the varieties of adipocire. The alkohol being repeatedly applied hot to the cerebral pulp previously dried, deposited each time on cooling brilliant laminæ of a yellowish white colour. This s stance was of an unctuous appearance, softened at. heat of boiling water, but did not melt. At a hig temperature it acquired a darker colour, and exhal during its fusion, an empyreumatic ammoniacal odour

From these results, Fourcroy concludes, that the ce bral pulp consists of a matter analogous to albumen, m oxygenized, and containing no fixed alkali, but hav certain phosphates in its composition. The matter of nerves is composed of the same substance.

CHAP. III.

OF THE DECOMPOSITION OF ANIMAL SUBSTANCES, FROM THE RE-ACTION OF THEIR ELEMENTS.

THE elements of which the greater number of animal substances are formed, having mutual energetic affinities, and the operation of these affinities being favoured by the state of condensation in which they exist, these substances are extremely liable to decomposition, from the re-action of their constituent parts, in consequence of which new combinations are formed. These may take place either at natural temperatures, or at temperatures more elevated; and according to either of these circumstances, the kind of decomposition, and the new combinations that are established, are different. In concluding the history of animal substances, both species of spontaneous decomposition are to be considered.

SECT. I.

OF THE DECOMPOSITION OF ANIMAL SUBSTANCES AT A HIGH TEMPERATURE.

WHEN any of the animal products is exposed to heat, its elements generally enter into binary or ternary combination. Nitrogen and hydrogen being those which are usually present in largest proportion, portions of them combine together, and form ammonia, which accordingly is always evolved. Another portion of the hydrogen enters into combination with carbon and oxygen, forming empyreumatic oil, acid, and oxy-carburetted hydrogen gas. Oxygen and carbon unite together, and form carbonic acid, with which the ammonia combines; and sulphur and phosphorus, which are generally in greater or less quantity constituents of animal matter, uniting with hydrogen, and probably also with certain proportions of nitrogen and oxygen, form those gases, having a foetid odour, the evolution of which peculiarly marks the decomposition of animal matter. These products are evolved in different proportions, and under various modifications, according to the composition of the substance decomposed. The residual charcoal contains usually salts, having lime, magnesia and soda for their bases, combined with phosphoric, sulphuric, muriatic, and carbonic acids, and also oxide of iron.

But besides these, which require no farther observations, a peculiar product is formed from the decomposition of many animal substances by heat, the Prussic Acid, the chemical history of which is still to be given. It appears to exist, as has already been stated, (page 365), fully formed in the vegetable kingdom, but, as obtained from animal substances, it is always the product of their decomposition by heat, and it is from this source that it is usually procured for chemical purposes.

A rich pigment had been known for a considerable time under the name of Prussian Blue. It is prepared by drying blood, and mixing three parts of the dried residuum with two parts of the potash of commerce, and calcining the mixture in a crucible by a red heat: it is then boiled in successive portions of water, which are afterwards mixed together, and concentrated by evaporation. A solution is prepared of one part of sulphate of iron, and two parts of alum; and to this the liquor obtained from the calcined blood and alkali is added, as long as any precipitate is formed. This precipitate is of a green colour, but by washing it with a little dilute muriatic acid, it becomes of a dark rich blue colour. This forms the prussian blue of commerce.

Much attention has been bestowed on the investigation of the nature of this substance. At an early period, after Woodward, in 1724, had made public the process, Brown and Geoffroy shewed, that other animal substances besides blood, as flesh, wool, &c. calcined with potash, furnished a ley capable of forming prussian blue, and ascertained some other facts connected with its formation.

Macquer made the most important discovery with regard to it,—that the property of forming the colour depends on a peculiar principle combined with the alkali; that in the formation of the prussian blue, this is transferred to the iron, and that it may be again abstracted from it by boiling the blue in an alkaline solution; the properties of the alkali are thus changed, and it acquires the power of again forming the precipitate of prussian blue, from a solution of sulphate of iron. He shewed likewise, that the reason the precipitate is thrown down green, is that the alkali is not entirely saturated with the colouring principle; the excess of alkali throws down, therefore, a portion of yellow oxide of iron from the sulphate, which mingling with the blue precipitate renders it green, and the muriatic acid gives the deep blue colour, by dissolving, and of course removing this oxide.

Scheele completed the investigation, and shewed the nature of this colouring principle, by obtaining it in a separate state. Having found, that when the liquor prepared from the calcined blood and potash is exposed to the air, it loses, in a short time, its power of precipitating iron blue; and farther, that when a quantity of this liquor is put into a vessel filled with carbonic acid gas, a piece of paper that had been dipt in a solution of sulphate of iron, being attached to the cork, this paper is soon covered with precipitated oxide of iron, and when wetted with muriatic acid, assumes a beautiful blue colour: he concluded, since acids thus appear to attract the alkali more strongly than the colouring matter does, and since this matter appears to be volatile, that it might be obtained by distillation. He therefore put a quantity of the alkaline liquor impregnated with it into a retort, with an excess of sulphuric acid, and distilled with a gentle heat. The water which came over had a peculiar smell and taste, and produced with oxide of iron a fine prussian blue. Exposed to the air for some hours, it entirely lost this property, the colouring principle being dissipated.

Scheele found it difficult, by single affinity, to transfer the colouring matter from prussian blue; for although the alkalis attract it, yet a portion of oxide of iron always accompanies it; and hence these compounds, as he remarks, are all triple salts, consisting of alkali, a little iron, and the colouring matter. With that skill, however, which eminently marked all his investigations, he discovered a process by which this may be effected, and which still affords us the best method of obtaining this principle in an insulated state. Two ounces of prussian blue, and one ounce of the red oxide of quicksilver prepared by nitric acid, are put into a flask, with six ounces of water, and boiled for some minutes, with constant agitation. It is then poured on a filtre, and the matter which remains on the paper, lixiviated with two ounces more of hot water. The liquid which has passed through, is a combination of the colouring matter with oxide of quicksilver, without any oxide of iron. This he found could not be decomposed, either by acids, alkalis, or lime; and the colouring matter could be separated only, by reducing the mercurial oxide to the metallic state. To effect this, the filtered solution, from the above quantities of materials, is poured on an ounce and a half of iron-filings free from rust, to which are added three drachms of sulphuric acid. The oxide of quicksilver is reduced to the metallic state. The clear liquor, after the action has ceased, is poured off and distilled. When the fourth part has come over, the whole of the colouring matter is obtained, as it is more volatile than water, and rises first. There is a slight contamination of sulphuric acid, which may be removed by distilling a second time from a little chalk *.

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* Scheele's Chemical Essays, p. 319.

Doubts have been entertained whether this principle can be regarded as an acid. Its taste, Scheele remarked, is not sour, but rather approaching to sweet, nor does it redden paper tinged with litmus. It has scarcely even the most important acid character, the power of neutralizing the alkalis and earths, and of forming with them crystallizable salts; or at least it acquires this power, as Berthollet has remarked, only when a metallic oxide enters at the same time into the combination. It has only the remaining equivocal acid characters, of being soluble in water, decomposing soap, and precipitating alkaline hydro-sulphurets; and, as the same chemist has observed, the name of acid can be given to it, rather from the properties it displays in its ternary combinations, than from those it has in its insulated state.

Prussic acid, under the form of its watery solution, has a strong odour, resembling that of the peach blossom. Its taste is sweetish and pungent; when pure it is colourless. In its action on the living system, it is highly narcotic, as has been already stated.

The volatility of this acid is such, that it easily escapes from its watery solution; and according to Bucholz, it is always partially decomposed by water. Like the other substances of animal origin, it is decomposed at a high temperature; though much less readily, as is evident from the fact, that it is formed only at the temperature of ignition. This may be considered even as giving to it a peculiar character.

Prussic acid combines with the alkalis and earths; but its affinity to them is inconsiderable, and hence the constitution of these compounds is easily subverted, water even producing their decomposition, especially when heated.

They are denominated Prussiates, and are best obtained in a state of purity, by combining the acid obtained by the process of Scheele, with the different bases. They have been little examined; a few observations only having been made with regard to them by this chemist *. With the fixed alkalis, he remarks, prussic acid forms a compound, which though it contain an excess of the colouring matter, still restores the blue colour of paper reddened by an acid. By distillation, part of the prussic acid is separated from it, and it is decomposed by all the acids, even by the carbonic. With ammonia a salt is formed, which has still the ammoniacal odour, even when the colouring principle is in excess; this salt rises by distillation, nothing but pure water remaining in the retort. The aqueous prussic acid dissolves but a small quantity of barytes; with lime it presents nearly the same results as with the alkalis, combining with it, and the compound being decomposed by heat, as well as by carbonic acid, on exposure to the air. Magnesia is dissolved by it in small quantity, but by exposure to the atmosphere, is again precipitated. Argil is not dissolved by it, in any sensible quantity.

Prussic acid has no sensible action on metals; but it acts on the oxides of some of them. Thus, oxide of gold becomes white; oxide of silver, precipitated by an alkaline carbonate from its nitrous solution, yields its carbonic acid with slight effervescence; oxide of quicksilver is dissolved, and the solution crystallizes in four sided prisms; oxide of copper assumes a citron colour, and oxide of cobalt a yellowish brown. The oxides of iron, tin, lead, and indeed the greater number of the other metals, are

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* Chemical Essays, 2d Dissertation on Prussian Blue.

not affected by it. It decomposes, however, some of the metallic salts: from a solution of nitrate of silver, a white powder is thrown down; from nitrate of mercury, a black powder; and from carbonate of iron, a precipitate at first of a sea-green colour, which changes to a blue.

By complex affinity, more striking effects are produced on the metallic salts. In examining these, Scheele employed prussiate of lime; and he gives the following enumeration of the changes it occasions. A solution of it being poured into a solution of gold, a precipitate is thrown down in a white powder, which is re-dissolved when the prussiate is added in excess, forming a colourless solution. The solution of platina is not changed: that of silver is precipitated of a white colour, and of a consistence like that of cheese; the precipitate being redissolved by an excess of the prussiate, and the combination in this case being so intimate, that it is not decomposed by muriatic acid. Mercury is precipitated from its nitrous solution in the form of a black powder. Sulphate of copper is precipitated of a citron colour; the precipitate being redissolved by an excess of the prussiate, and forming a colourless liquor, as it does also when submitted to the action of liquid ammonia. Sulphate of zinc gives a precipitate of a white colour; and this, unlike the greater number of these precipitates, is soluble in acids. Sulphate of iron is precipitated first of a yellowish brown colour, which soon changes to green, and then becomes blue on the surface, as it does also immediately on adding an acid. From acetate of lead, a white powder is precipitated; from the solution of cobalt, a powder of a brownish yellow colour; neither of these being redissolved by an excess of acid. Similar compounds are established by prussiate of potassa added to the metallic solutions. It is probable, that the greater number of them are triple combinations; the prussic acid, with part of the salifiable base, entering into combination with the metallic oxides, the prussic acid having a tendency to form such ternary combinations: hence, as Berthollet has remarked, the super-natant liquid retains an excess of acid, though the prussiate by which the metallic salt is decomposed contain more alkali than is requisite to its saturation, and the precipitate weighs more than it could do if the oxide alone were combined with the prussic acid. These combinations are much more permanent than the pure prussiates, the metallic oxide exerting such an affinity to the prussic acid, as to preserve it from decomposition.

Of these ternary combinations, those with oxide of iron are of importance, from their use as chemical tests, and as forming prussian blue. The liquor which is obtained by digesting an alkaline solution on prussian blue is of this nature, a portion of iron being always contained; and hence, when an acid is added so as to saturate part of the alkali, a precipitate of prussian blue is formed. And when the solution is added to a solution of iron, a portion of this iron in the state of oxide enters into the combination, forming a similar precipitate, while the alkali is partly attracted by the acid with which the iron was combined.

The nature of these combinations is, however, considerably diversified by the state of the iron with regard to oxidizement, as Proust more particularly pointed out *. If it exists in combination with an acid at the minimum of oxidizement, the precipitate formed, by adding the

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* Nicholson's Journal, 4to, vol. i. p. 454.

common prussiate of potassa and iron, is of a white colour, but from exposure to the air, it very soon acquires a blue shade; or, if the metal be at a higher state of oxidizement, the precipitate is at the first blue. Generally, however, as thrown down from the solution of iron, if no acid be present, it is of a green colour; owing, as has been already explained, to the difficulty of saturating the alkali with the prussic acid; and hence, by the portion of alkali which is present in excess, a quantity of yellow oxide is precipitated, which gives to the blue prussiate a yellow colour. This is prevented when the solution of iron has an excess of acid; or the green precipitate assumes a blue, when this oxide is removed by washing with a diluted acid. It thus appears, that there are various prussiates of potassa and iron, differing both in the proportions of the alkali and the oxide to the acid, and in the degree of oxygenizement of the metal. According to Berthollet, however, the distinction between the white and the blue prussiates does not depend merely on this cause, but rather on the force of affinity exerted by the acid to the oxide of iron in its different degrees of oxidizement, and which is therefore capable of being varied by causes which do not change the state of oxidation, as by water or by the acids, of which he gives examples *.

The triple prussiate which is obtained by boiling an alkaline solution on prussian blue, has been much used by chemists as a test to discover the presence of iron, it being a delicate one, from the deep blue colour which it strikes with the iron at the maximum of oxidizement. As

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* Chemical Statics, vol. ii. p. 215.

it always contains, however, a portion of iron, it is liable to fallacy; for if any free acid be present, or be evolved in the application of the test, this re-acts upon it, and gives rise to a precipitate of prussian blue, indicating, of course, iron to be present when it is not. Chemists have endeavoured to remove this source of fallacy, by freeing it from this portion of iron; but it does not appear, that by any process it can be entirely abstracted. Richter and Bucholz have even concluded, from their investigations, that the presence of the oxide of iron is essential to preserve the constitution of the prussic acid; that the compound of this acid and the alkali alone, can be formed only in the dry way, and at the temperature of ignition: when it is dissolved in water, it is immediately decomposed; part of the prussic acid escapes, and, from the smell of ammonia produced, part appears to be decomposed: it is only from the presence of oxide of iron that the combination is established; and it is more permanent, as the proportion of this is larger. All the precipitates produced by means of the test prepared in the usual method, they conclude, contain iron, and are different in their colour from those where the iron is not present *.

It appears, however, that when the triple prussiate of potassa and iron contains only a certain quantity of the metal, this exists in the combination with such force of attraction, that even a free acid does not subvert it, or produce prussian blue; and that, therefore, a triple prussiate of this nature may be formed, which may be employed with more accuracy as a test of iron. The liquor

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* Nicholson's Journal, vol. ix. p. 278.
Annales de Chimie, tom. li. p. 180.

which is prepared from the mixture of blood and pearl-ash calcined, is, under this point of view, preferable to that prepared from the action of an alkaline ley on prussian blue; for although the former contains a portion of oxide of iron derived from the blood, yet it is much less considerable than that which the latter contains. The proportions, according to Bucholz, which answer best in preparing the triple prussiate with this view, are two parts o dried blood with one of carbonate of potassa; this mixture being heated to redness in a crucible, and being kept in a state of ignition for three quarters of an hour after the flame that appears at the surface has ceased. This, dissolved in water, affords a liquor which contains only a small quantity of iron, and which, dropt into muriatic acid, affords no blue, but only a white precipitate *.

Even the common solution of triple prussiate of potassa, and iron prepared by digesting an alkaline solution with prussiate of iron, may be so far freed from the metal, as to be used as a test. A process of this kind employed by Klaproth has been described by Mr Kirwan †. The most essential circumstance appears to be crystallizing the compound. The liquor is filtered, and any excess of alkali saturated by the addition of sulphuric acid; (or, as Richter has since proposed, by acetate of lime:) it is poured off clear from a precipitate which is thrown down, and is evaporated, so that, when set aside, it shall crystallize: crystals of a cubic form and of a yellowish colour are found mingled with crystals of sulphate of potassa, and with oxide of iron. The former are picked out, and

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* Nicholson's Journal, vol. ix. p. 280.

† Elements of Mineralogy, vol. i. p. 494.

redissolved in water: any sulphuric acid that may be present is removed by the addition of barytic water, and is again made to crystallize. These crystals are dried and kept for use: if they receive no bluish tinge when wetted with muriatic acid, they may be considered as sufficiently pure to be employed as a test. In judging, however, of the *quantity* of iron contained in the precipitate which they may throw down from any liquor containing this metal, allowance must be made for the portion of it which they contain: this is done by decomposing 100 grains of the crystallized salt, by exposure to a strong red heat, discovering what quantity of oxide of iron remains, and from this, by knowing what quantity of the salt has been employed in the precipitate, determining that quantity of the iron which it indicates has been derived from this source. In general, the crystallized salt, as prepared in this method, contains from 22 to 30 in 100 parts of oxide of iron. Berthollet has observed, that it is more constant in its composition, if it be calcined lightly previous to the second crystallization; the oxide not essential to the composition being thus more effectually separated.

The triple prussiate is also, in the common method of preparing it, generally impure, from a mixture of sulphate of potassa, derived from the potash of commerce, from which it has been prepared; and this is the source of a mistake, which at one time prevailed among chemists; that barytes is precipitated copiously by this test from its saline solutions. This may be removed by the action of barytes; and on this Dr Henry has founded a process for preparing a purer triple prussiate than by the common methods.* It consists in adding prussian blue to a solution of pure barytes in water, until it cease to be discoloured.

The solution is filtered, so as to free it from any deposite of oxide of iron: after it has stood some hours, yellowish crystals of prussiate of barytes and iron form, and another quantity is obtained by evaporation of the liquor. These crystals, in powder, are added to a solution of carbonate of potassa gently heated, until the solution no longer restores the colour of reddened litmus paper: after digesting the mixture for half an hour, the liquor is filtered, and, when evaporated, affords well-formed crystals. They still contain about 0.24 of oxide of iron; but a considerable part of this may be abstracted, by digesting the solution, before evaporating it, with a little acetic acid *.

The Prussian Blue of commerce, besides its essential principles, contains always a quantity of argil. This is derived from a quantity of alum, dissolved along with the sulphate of iron, previous to the precipitation of this by the addition of the ley from calcined blood and potash; and serves the purpose merely of diluting the very deep colour, and giving more consistence to the pigment.

The common prussiate of potassa and iron not only precipitates iron from its solution, but the greater number of the other metals, all of them, indeed, except platina, antimony, and tellurium; and thus affords a test useful in discovering the metals.

Besides the triple compounds of prussic acid, potassa, and oxide of iron, other ternary combinations are formed with the other salifiable bases. That of barytes, the properties of which have been pointed out by Dr Henry, has been already noticed. It is crystallizable: the crystals are

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* Nicholson's Journal, 4to, vol. iv. p. 31.

rhomboidal, and have a yellow colour; they are sparingly soluble in water; four ounces, at 65°, not dissolving more than one grain, and only between five and six grains at 212°. The prussiate of strontites and iron is less disposed to crystallize; the dry mass obtained by evaporation is readily soluble in water; one ounce, at 65°, dissolving 120 grains *. The prussiate of lime and iron is deposited, by evaporation of its solution, in minute crystals of a yellowish tinge. The others are scarcely known.

The compound formed from the precipitation of the salts of copper by the triple prussiates is of a fine brown colour: it has been introduced as a paint by Mr Hatchet, and found superior to every brown paint now in use in beauty and intensity. The deepest colour is obtained from the muriate of copper, precipitated by the prussiate of lime and iron; the muriate being dissolved in ten parts of distilled water, and the solution of the prussiate added as long as there is any precipitation †.

From the origin of prussic acid, it may be inferred to consist of the elements that usually form the animal products. This is confirmed by the results of its analysis. It was known, that prussian blue, decomposed by heat, afforded ammonia; and Scheele found, that it was yielded also by the other prussiates, with carbonic acid gas and residual charcoal. The state of chemistry at that period did not allow of the proper conclusion being drawn, and Scheele merely inferred, that prussic acid consists of ammonia and an oily matter. He added, however, an instructive synthetic experiment. He mixed equal parts of

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* Nicholson's Journal, 4to, vol. iii. p. 171.

† Journals of the Royal Institution, vol. i. p. 306.

charcoal-powder and sub-carbonate of potassa, and raised them in a crucible to a red heat. He then thrust to the bottom of the crucible nearly the same proportion of muriate of ammonia, in small pieces: in two minutes, the production of ammoniacal vapours had ceased, and the matter was immediately lixiviated with hot water. It afforded a ley, which copiously precipitated prussian blue from sulphate of ammonia. A similar, though less perfect result, was obtained when he substituted plumbago. And from these it appears, as he remarks, that volatile alkali, with carbonaceous matter, can afford prussic acid *. No farther inference could be drawn while the nature of ammonia was unknown.

Berthollet, when he had discovered the composition of ammonia, applied the discovery to the theory of the formation of prussic acid, and inferred, that this is formed from the elements of the ammonia—nitrogen and hydrogen entering into combination with a portion of carbon, and that it is therefore a triple compound of these principles †. This has been confirmed by a variation in the mode of performing the synthetic experiment of Scheele, executed by Clouet; passing ammonia in the gaseous form, disengaged from a mixture of muriate of ammonia and quicklime, through a tube filled with charcoal and kept at a full red heat: the gas is received at the extremity of the tube in bottles containing water, or an alkaline solution; and pure prussic acid is found at the end of the experiment ‡.

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* Chemical Essays, p. 403.

† Mémoires de l'Acad. des Sciences, 1786, p. 148.

‡ Annales de Chimie, tom. xi. p. 30. Journal de l'Ecole Polytechnique, tom. ii. p. 12[illegible]

It has been considered as doubtful, whether oxygen enters into the composition of this acid. Berthollet rather supposed that it did not, or that it contained only a small proportion, from finding, that in its decomposition the gas disengaged was chiefly carburetted hydrogen, and not carbonic acid. All the species of carburetted hydrogen, however, no doubt contain oxygen in their composition; carbonic acid, too, is produced in a certain quantity, as Scheele observed; and Vauquelin has remarked, that however dry a prussiate may be when subjected to decomposition by heat, carbonate of ammonia is always produced. It can scarcely be doubted, therefore, that oxygen enters into its composition; and accordingly, Vauquelin has observed, that in the formation of it from ammonia and charcoal, the quantity is much increased if a substance be added which can afford oxygen. Thus, if oxide of lead be employed instead of lime to decompose the muriate of ammonia when it is heated in a state of mixture with charcoal, the product of prussic acid is augmented in the proportion even of six to one *.

Berthollet, in his experiments on this substance, observed, that when it was submitted to the action of oxymuriatic acid, it suffers a chemical change, receiving oxygen, and the oxymuriatic passing to the state of muriatic acid. It is not very clear, whether in this case the prussic acid merely receives a portion of oxygen into its composition, or whether the oxygen combines with its hydrogen or carbon only. The acid in this state acquires a stronger smell, becomes more volatile, and appears to

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* Manual of Chemistry by Lagrange, vol. ii. p. 358.

exert less energetic affinities to the alkalis: it precipitates iron green from its solutions; and this precipitate becomes blue from exposure to light, or from the action of sulphurous acid, or iron. If it be still more impregnated with oxymuriatic acid, and be then exposed to the light of the sun, it appears entirely to change its nature: it separates in the form of an oily-like matter, of an aromatic odour, which subsides to the bottom of the vessel, and which, if converted into vapour by the application of heat, still refuses to unite with water, or with oxide of iron. When the acid is in that state in which it forms a green precipitate with iron, if lime or an alkali be added to this precipitate, ammonia is evolved.

SECT. II.

OF THE SPONTANEOUS DECOMPOSITION OF ANIMAL SUBSTANCES AT LOW TEMPERATURES.

WHEN the affinities of the elements of dead animal matter are allowed to operate by that degree of humidity or softness which these substances usually have, new combinations are established even at natural temperatures, which continue to proceed until the animal substance is entirely decomposed. Changes of this kind constitute the general process of Putrefaction; though they are also considerably varied, according to the circumstances under which they take place, and, in particular, according to the presence of air and humidity.

If animal matter be entirely excluded from these two agents, in other words, if it be completely dried and secluded from the atmosphere, it decays very slowly, any sensible chemical decomposition not being produced in it for a very great number of years.

If those animal substances which are not soluble in water, those, for example, which consist principally of fibrin, as the muscular fibre or flesh, be kept compressed, or be immersed in water, as the air is thus nearly excluded, the series of changes are modified, and the fibrin is ultimately converted into a substance of a fatty nature, having indeed nearly all the properties of spermaceti.

This species of decomposition was first particularly observed on the occasion of the removal of a burying ground in Paris, containing common graves, or repositories destined for the poor, in which, with a singular indifference, a number of bodies were accumulated together. It was known to the grave-diggers, that after a number of years, they were converted into a species of fatty matter. Fourcroy examined the appearances presented, and has given a memoir on the subject*, to which, or a full view of it by Mr Nicholson †, I refer. It has since been shewn by Dr Gibbes, that when the flesh of animals is immersed under water, it is converted into a similar fatty matter; in a piece of lean beef, secured in a running stream, the conversion was effected in the course of a few months; and it was also produced by the agency of dilute nitric acid ‡. In these cases, part of the nitrogen and hydrogen appear to combine together and form ammonia, which is found in the fatty matter, while another portion of hydrogen with carbon, and a proportion of oxygen, form the fat.

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* Annales de Chimie, tom. v. p. 154.

† Nicholson's Dictionary, vol. ii. p. 861.

‡ Philosophical Transactions, 1794, 1795.

When the atmospheric air is admitted to animal substances, and moisture is present, the process more strictly named Putrefaction takes place. This has been defined, that species of decomposition or change in the mixture of organic matters, by which ammonia and a particular effluvium of a most offensive smell, called Putrid, are formed. It takes place only in those substances which, besides carbon and hydrogen, contain nitrogen and phosphorus: such are the animal products and vegetable gluten.

The circumstances more peculiarly favourable to it, are a due degree of heat and moisture and access of air. A temperature from 60° to 80° of Fahrenheit, best favours its progress: by intense cold it is entirely checked.

When this process first commences, the matter emits a slightly offensive smell, which soon becomes extremely fœtid; the taste likewise becomes nauseous: the colour is greenish: the firmness and cohesion of the substance are soon diminished, and at length it becomes soft and pulpy; its smell becoming more and more offensive. It thus continues, losing weight, until the putrefaction is completed, and little remains but an earthy residuum.

In this process then, the putrefying matter is resolved into new compounds, which escape in the gaseous form. The precise nature of these combinations has not, from the extreme offensiveness of the process, been accurately ascertained. And they probably vary somewhat according to the nature of the animal substance, and the circumstances under which the putrefaction takes place. Ammonia is formed by the union of the nitrogen and hydrogen of the animal matter, and frequently also acetic acid, by which it is neutralized. Phosphuretted hydrogen is disengaged, since this gas, even when obtained pure, has in a very great degree the odour named Putrid; and it has often been observed, that animal matter during putrefaction has appeared luminous. Sulphuretted hydrogen makes another part of the vapours disengaged from putrefying substances; as these vapours have in some degree its smell, and are capable of blackening the metals, a peculiar property of this gas. Lastly, carburetted or oxycarburetted hydrogen and carbonic acid are evolved. It is probable too, that not only these binary combinations, but compound gases, consisting of three or more of these elements with oxygen, are formed and disengaged.

This change then, is nothing more than the elements of the animal substance entering into new combinations, which pass off in the gaseous form, the earthy and saline matter forming the residuum.

Putrefaction is the great process employed by nature, to separate the principles which vegetation and animalization had combined, and thus to be subservient to their recomposition. It is a process which must always go on at the surface of the earth; its products are diffused through the atmosphere, absorbed by water, or taken up by the soil. They furnish the principal nutritious matter for the support and growth of vegetables, and they are thus again brought into new combinations, which are prepared for assimilation in the animal system.

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